

General Disclaimer

One or more of the Following Statements may affect this Document

- This document has been reproduced from the best copy furnished by the organizational source. It is being released in the interest of making available as much information as possible.
- This document may contain data, which exceeds the sheet parameters. It was furnished in this condition by the organizational source and is the best copy available.
- This document may contain tone-on-tone or color graphs, charts and/or pictures, which have been reproduced in black and white.
- This document is paginated as submitted by the original source.
- Portions of this document are not fully legible due to the historical nature of some of the material. However, it is the best reproduction available from the original submission.

NASA-CR-134958
January 1976

(NASA-CP-134958) FABRICATION PROCESS
DEVELOPMENT OF SiC/SUPERALLOY COMPOSITE
SHEET FOR EXHAUST SYSTEM COMPONENTS
Technical Report, 15 Jul. 1974 - 31 Oct.
1975 (Westinghouse Electric Corp.) 47 p HC G3/24 13653

N76-17202
HC \$ 4.00
Unclassified



FABRICATION PROCESS DEVELOPMENT OF SiC/SUPERALLOY
COMPOSITE SHEET FOR EXHAUST SYSTEM COMPONENTS

b..

J. A. Cornie, C. S. Cook and C. A. Andersson

Westinghouse Electric Corporation

prepared for

National Aeronautics and Space Administration

NASA-Lewis Research Center
Contract NAS3-18921
R. Barrows, Project Manager



1. Report No. NASA-CR-134958	2. Government Accession No.	3. Recipient's Catalog No.	
4. Title and Subtitle FABRICATION PROCESS DEVELOPMENT OF SiC/SUPERALLOY COMPOSITE SHEET FOR EXHAUST SYSTEM COMPONENTS		5. Report Date January 1976	
7. Author(s) J.A. Cornie, C.S. Cook and C.A. Andersson		6. Performing Organization Code	
9. Performing Organization Name and Address Westinghouse Electric Corporation Research and Development Center Pittsburgh, Pennsylvania 15235		8. Performing Organization Report No.	
12. Sponsoring Agency Name and Address NASA-Lewis Research Center		10. Work Unit No.	
		11. Contract or Grant No. NAS3-18921	
		13. Type of Report and Period Covered July 1974-November 1975	
		14. Sponsoring Agency Code	
15. Supplementary Notes			
16. Abstract A chemical compatibility study was conducted between SiC filament and the following P/M matrix alloys: Waspaloy, Hastelloy-X, NiCrAlY, HA-188, S-57, FeCrAlY and Incoloy 800. None of the couples demonstrated sufficient chemical compatibility to withstand the minimum HIP consolidation temperatures (996°C) or intended application temperature of the composite (982°C). However, Waspaloy, Haynes 188, and Hastelloy-X were the least reactive with SiC of the candidate alloys. Chemical vapor deposited tungsten was shown to be an effective diffusion barrier between the superalloy matrix and SiC filament providing a defect-free coating of sufficient thickness. However, the coating breaks down when the tungsten is converted into intermetallic compounds by interdiffusion with matrix constituents. Waspaloy was demonstrated to be the most effective matrix alloy candidate in contact with the CVD tungsten barrier because of its relatively low growth rate constant of the intermediate compound and the lack of formation of Kirkendall voids at the matrix-barrier interface. Fabrication methods were developed for producing panels of uniaxial and angle ply composites utilizing CVD tungsten coated filament. The matrix was in the form of a powder cloth which was held intact with a fugitive PMMA binder. Tensile testing of the composite specimens revealed that composite mechanical integrity will be directly related to the ability to prevent chemical interaction between the fiber and matrix.			
17. Key Words (Suggested by Author(s)) composites, superalloys, silicon carbide, filament, compatibility, diffusion, barriers, mechanical properties		18. Distribution Statement Unclassified Unlimited	
19. Security Classif. (of this report) Unclassified	20. Security Classif. (of this page) Unclassified	21. No. of Pages	22. Price*

* For sale by the National Technical Information Service, Springfield, Virginia 22151

TABLE OF CONTENTS

	<u>Page</u>
FOREWORD.	i
ABSTRACT.	ii
SUMMARY	iii
ACKNOWLEDGMENTS	iv
1. INTRODUCTION.	1
2. PRELIMINARY SCREENING EVALUATION.	2
2.1 Preliminary Characterization of Matrix Alloys.	2
2.2 Matrix Alloy - SiC Filament Compatibility.	4
2.2.1 Matrix Screening.	4
2.2.2 Discussion of Uncoated SiC/Matrix Compatibility	6
2.2.3 Diffusion Barrier Studies	8
2.2.4 Matrix Alloy Selection.	10
3. COMPONENT CHARACTERIZATION.	12
3.1 Matrix Mechanical Properties	12
3.2 Tensile Strength of SiC Filament	15
4. COMPOSITE FABRICATION	17
4.1 Composite Design	17
4.2 Binder Removal	18
4.3 Composite Panel Fabrication.	18
5. MECHANICAL PROPERTY EVALUATION.	21
6. DISCUSSION OF RESULTS	23
7. SUMMARY OF RESULTS.	24
8. REFERENCES.	26
FIGURES	

FOREWORD

This technical report describes work performed for NASA-Lewis Research Center under Contract NAS3-18921 during the period 15 July 1974 to 31 October 1975. It was submitted by the authors in December 1975. The contract with the Metallurgy and Metals Processing Department of the Westinghouse Research Laboratory, Westinghouse Electric Corporation, Pittsburgh, PA 15235, under the technical direction of Dr. Richard Barrows of the NASA-Lewis Research Center, Cleveland, Ohio.

Westinghouse personnel contributing to this program are: Dr. J. A. Cornie, Program Manager, Dr. C. A. Andersson, and Mr. J. W. Salatka, Composite Fabrication and Evaluation, Messrs. C. S. Cook and R. Lovic, Hot Isostatic Pressing, Mr. D. A. Kaminski, Composite Fabrication and Filament Testing, and Mr. G. A. Blann and C. W. Hughes, Metallography and SEM evaluations.

ABSTRACT

A chemical compatibility study was conducted between SiC filament and the following P/M matrix alloys: Waspaloy, Hastelloy-X, NiCrAlY, HA-188, S-57, FeCrAlY and Incoloy 800. None of the couples demonstrated sufficient chemical compatibility to withstand the minimum HIP consolidation temperatures (996°C) or intended application temperature of the composite (982°C). However, Waspaloy, Haynes 188, and Hastelloy-X were the least reactive with SiC of the candidate alloys.

Chemical vapor deposited tungsten was shown to be an effective diffusion barrier between the superalloy matrix and SiC filament providing a defect-free coating of sufficient thickness. However, the coating breaks down when the tungsten is converted into intermetallic compounds by interdiffusion with matrix constituents. Waspaloy was demonstrated to be the most effective matrix alloy candidate in contact with the CVD tungsten barrier because of its relatively low growth rate constant of the intermediate compound and the lack of formation of Kirkendall voids at the matrix-barrier interface.

Fabrication methods were developed for producing panels of uniaxial and angle ply composites utilizing CVD tungsten coated filament. The matrix was in the form of a powder cloth which was held intact with a fugitive PMMA binder.

Tensile testing of the composite specimens revealed that composite mechanical integrity will be directly related to the ability to prevent chemical interaction between the fiber and matrix.

SUMMARY

A chemical compatibility study was conducted between SiC filament and the following argon atomized P/M matrix candidate alloys: Waspaloy, Hastelloy X, NiCrAlY, HA-188, S-57, FeCrAlY, and Incoloy 880. None of the SiC-matrix candidate alloy couples demonstrated sufficient chemical compatibility to withstand the minimum hot isostatic pressing temperature of 996°C or the intended maximum operation temperature of 982°C. However, Waspaloy, Haynes Alloy 188, and Hastelloy X were the least reactive with SiC of any of the candidate alloys, and warranted further consideration as matrix candidates with barrier coated SiC filament.

Chemical vapor deposited (CVD) tungsten was shown to be an effective interim choice as a diffusion barrier between the superalloy candidates and SiC filament providing the coating is defect free and of sufficient thickness. The diffusion barrier loses its effectiveness when the free tungsten is consumed in intermetallic compound formation with matrix constituents. The growing intermetallic compound layer finally makes contact with the SiC filament and transforms into the various possible silicides, thus deteriorating the filament. Waspaloy was shown to be the most effective matrix alloy candidate in contact with the CVD tungsten barrier because of the low growth rate constant of the intermediate compound formation and the lack of formation of Kirkendall voids at the matrix-barrier interface. An analysis of projected life based on growth rate of the intermediate compounds, required thickness of the CVD W barrier, and resultant density increase is presented.

Fabrication methods were developed for producing panels of uniaxial and angle ply composites utilizing CVD W coated SiC filament and the matrix alloy (Waspaloy) in the form of argon atomized powder consolidated into a powder tape or cloth with a fugitive PMMA binder.

Initial tensile testing of composite specimens revealed that even small amounts of chemical interaction between the matrix and filament will seriously degrade the mechanical properties of the composite. Any improvement in composite properties will be directly proportional to improvements in filament coating integrity.

ACKNOWLEDGMENTS

The technical assistance of the following individuals are gratefully acknowledged: I. Ahmad of Watervliet Arsenal for providing CVD tungsten coated SiC filament, V. Kurkonis and H. DeBoldt of AVCO for information and advice on filament testing and handling, R. Lovic for Hot Isostatic Pressing, J. Salatka for Design and Fabrication Assistance, and D. Kaminski for Fabrication and Filament Testing.

1. INTRODUCTION

Ni base superalloys are used extensively for exhaust system components of commercial and military gas turbine engines. Advanced supersonic engines will require more than 3000 lbs. of superalloy sheet as nozzles, noise suppressors, and thrust reverser components if present generation materials are utilized. Reduction in this weight would be possible if materials were available possessing a higher specific strength than the presently developed superalloys. Alloy development efforts toward optimizing strength, fabricability, oxidation, and corrosion resistance are being exhausted. Fortunately, other approaches are available. The use of high strength, low density fibers such as SiC in a superalloy matrix forming a composite material, could result in as much as 30% reduction in weight of these components. This weight savings can be directly translated into improved aircraft performance or payload.

Silicon carbide has been selected because of its low density and high strength at 982°C (1800°F), the design temperature. The stated objective of this program is to develop processes for fabrication of SiC fiber/superalloy matrix composite panels. In order to achieve the stated goals, a consolidation process must be optimized to the point that chemical interaction (and hence loss of strength) during fabrication and service at 982°C (1800°F) is eliminated. Thermal incompatibility due to thermal expansion mismatch between fiber and matrix must also be evaluated. Finally processing methods must be developed and evaluated for the fabrication of scale-up panels of uniaxial and angle-ply configurations.

This program has demonstrated the fundamental incompatibility between uncoated SiC fiber and the matrix during fabrication, even at temperatures as low as 995°C (1825°C). Chemical vapor deposited tungsten coated SiC filaments have been successfully consolidated into Waspaloy, HA-188, and Hastelloy-X. However, prolonged heating at 982°C (1800°F) resulted in interdiffusion between the HA-188 and Hastelloy-X alloys resulted in Kirkendall void formation at the CVD W/matrix interface. Waspaloy was then chosen as the matrix material for further fabrication evaluation.

The selection of tungsten as a diffusion barrier must be considered as interim in that fabrication and testing techniques may be developed on CVD W coated wire. However, the high density of tungsten becomes an important consideration in view of the stated goals, i.e., weight reduction. Fortunately other less dense barriers appear feasible and can be developed once the composite feasibility is demonstrated with presently available tungsten barriers.

2. PRELIMINARY SCREENING EVALUATION

2.1 Preliminary Characterization of Matrix Alloys

The matrix alloys were chosen from Fe, Co and Ni base systems on the basis of oxidation resistance, ductility, strength and fabricability. As many different types of materials from the three base systems (i.e., solid solution vs γ' precipitation hardness) were chosen as possible in order to evaluate the potential for developing compatibility with silicon carbide.

All alloys were purchased in the form of argon atomized powder and thin sheet or foil, fabrication permitting. The alloys selected, their purchased form and vendor, are listed in Table 1.

TABLE 1

No.	Alloy Design.	Form		Vendor
		Powder	Foil	
1	Waspaloy	X	X	Kelsey-Hayes Stellite
2	Hastelloy X	X	X	Alloy Metals, Inc. Stellite
3	NiCrAlY	X		Kelsey-Hayes
4	Haynes 188	X	X	Alloy Metals, Inc. Stellite
5	G.E. 1541 (FeCrAlY)	X		Kelsey-Hayes
6	IN-800	X	X	Alloy Metals, Inc. Williams & Co.
7	S-57	X		Alloy Metals, Inc.

The vendor chemical analyses of the as-received powder or sheet material are given in Table 2. A tap density and mesh range analysis of the as-received powder is given in Table 3. The tap density is an important parameter when calculating filling volumes and volume fractions in subsequent composites. From past experience, we have found that the packing density in powder tape is the same as the tap density of bulk powder.

TABLE 2. VENDOR ANALYSIS (wt. pct.)

<u>Alloy</u>	<u>Ni</u>	<u>Cr</u>	<u>Co</u>	<u>Fe</u>	<u>W</u>	<u>Mo</u>	<u>Al</u>	<u>Ti</u>	<u>Zr</u>	<u>Ta</u>	<u>C</u>	<u>N</u>
Waspaloy - (Powder)	bal	19.88	13.67	0.89		4.57	1.46	3.03	0.06		0.053	
- (Sheet)	bal	19.1	13.6	1.37		4.44	1.50	2.96	0.05		0.08	
- (Nominal)	bal	19.5	13.5	2.0		4.25	1.3	3.0	0.085		0.1	
Hastelloy X (Powder)	bal	21.39	0.92	18.51	0.53	9.96					0.01	
(Sheet)	bal	21.6	1.88	19.32	.56	9.11					0.07	
(Nominal)	bal	20.5-23	0.5-2.5	17-20	0.2-1	8-10					0.15	
NiCrAlY (Powder)	bal	16.31		.005			5.47				.009	17 ppm
(Nominal)	bal	18					6.0					
Haynes 188 (Powder)	21.85	22.26	bal	0.78	15.04						0.01	
(Sheet)	22-37	22.58	bal	1.96	14.06						0.11	
(Nominal)	22	22	36	3	14.5						0.1	
S-57 (Powder)	10.16		bal				3.53				5.09	
(Nominal)	10		bal				3					
FeCrAlY (Powder)		24.2		bal			3.99					
(GE 254) (Nominal)		25		bal			4					
Incoloy 800 (Powder)	32.10	19.78		bal			0.25	0.46			0.12	
(Sheet)	33.17	19.58		44.75			0.29				.03	
(Nominal)	30-35	19-23		bal			0.15-0.6	0.15-0.6			0.1	

<u>Alloy</u>	<u>O₂</u>	<u>B</u>	<u>Ta</u>	<u>Mn</u>	<u>Si</u>	<u>Other</u>
Waspaloy (Powder)	95 ppm	0.006		0.05	0.10	0.01 S, 0.05 Cu, 0.002 P
(Sheet)		0.005		0.02	0.05	< .005 S, .009 P, 0.01 Cu
(Nominal)		0.005				
Hastelloy X (Powder)	600 ppm			0.42	0.45	
(Sheet)				0.61	0.4	< .005 S, .02 P
(Nominal)						
NiCrAlY (Powder)	96 ppm				54 ppm	20 ppm S, .21 Y, 10 ppm P 0.5 Y
(Nominal)						
Haynes 188 (Powder)	420 ppm			0.17	0.37	0.055 La
(Sheet)				.70	0.42	.03 La, .007 S, .01 P
(Nominal)				1.25	0.35	0.9 La
S-57 (Powder)	224 ppm					0.55 Y
(Nominal)			5			0.5 Y
FeCrAlY (Powder)	104 ppm					0.73 Y
(GE 254) (Nominal)						1.0 Y
Incoloy 800 (Powder)	314 ppm			< 0.10	< 0.10	< 0.10 Cu, .005 S
(Sheet)				0.83	0.34	.007 S, 0.57 Cu
(Nominal)					1.5	

TABLE 3

<u>Alloy</u>	<u>Mesh Range</u>	<u>Tap Density</u>	<u>Oxygen ppm</u>
Waspaloy	100% - 325	58.2%	95
Hastelloy X	49.4% + 325 50.6% - 325	64.0	600
NiCrAlY	100% - .60+100	55.7	
Haynes 188	72.6% + 325 27.4% - 325	63	420
S-57	19.8% + 100 51.5% - 100+325 28.7% - 375	60	
FeCrAlY	100% - 325	57.1	104
Incoloy 800	54.1% + 325 45.9% - 375	59	314

The powder morphology of the various alloys are shown in SEM photographs in Figs. 1-7. These photographs show the powder to be primarily spherical in shape with a wide distribution of powder sizes even within the -325 mesh size. Occasional oxide scale is noted in some of the powders with higher oxygen levels (Figs. 2, 4 and 7).

2.2 Matrix Alloy - SiC Filament Compatibility

2.2.1 Matrix Screening

The first criteria for compatibility screening is the ability of the matrix-filament combination to withstand the HIP process. The first step in the investigation was to determine the minimum parameters for matrix consolidation. Metallographic analysis of hot isostatic pressed powders showed that adequate consolidation occurred for all alloys at temperatures above 996°C (1825°F) at a pressure of 103.4 MPa (15 ksi) with a hold time at temperatures of two hours.

Compatibility specimens for the HIP screening study were prepared by loading several hundred 4 cm (10 inch) long, 0.010 cm (0.004 in) diameter SiC filaments into a 0.635 cm (0.25 inch) ID 316 stainless steel capsule filling with the matrix candidate alloy powder and evacuating to 5×10^{-5} torr while heating to 371°C (700°F). The capsules were sealed by hot forging and weld sealing. The matrix powder was consolidated around the filaments by HIP at 996°C (1825°F) and 1093°C (2000°F) at the above mentioned time and pressure.

Extensive chemical interaction between the SiC filament and the various matrix candidate alloys was noted after the 996 and 1093°C HIP consolidation temperatures although the interaction was clearly greater for some alloys than others. Photomicrographs of the chemical interaction of the various combinations are given in Figs. 8-14 for the 996°C (1825°F) HIP consolidation temperature.

The severity of interaction expressed as the thickness of the interaction zone and as the volume fraction of unreacted fiber are shown in Fig. 15. The following observations may be summarized from an inspection of Figs. 8-15:

(1) None of the candidate alloys in the powder form limited chemical interaction during fabrication, although Haynes Alloy 188 (Co base), Waspaloy and Hastelloy-X (Ni base) were clearly superior to the remaining candidates.

(2) The matrix was embrittled in all cases by the chemical interaction as evidenced by the cracking which presumably occurred during cooling. This cracking gives evidence to the existence of thermal-expansion-differential stresses.

(3) Full consolidation of the matrix around the filaments occurred at 996°C (1825°F).

The following conclusions resulted from the above observations:

(1) Excessive chemical interaction cannot be avoided for the systems evaluated at processing temperatures of 996°C or greater.

(2) Any attempt to consolidate at temperatures below 996°C (1825°F) would be undesirable since the intended operation temperature of the composite is only a few degrees lower (982°C (1800°F)).

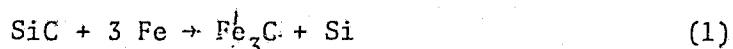
(3) Since long time compatibility is impossible, a diffusion barrier between the filament and matrix is required.

Regardless of the diffusion barrier employed, a certain inherent (though inadequate) compatibility is desirable. The Haynes Alloy 188, Waspaloy, and Hastelloy-X alloys were selected as the matrix candidates for further compatibility evaluation with a diffusion barrier.

2.2.2 Discussion of Uncoated SiC/Matrix Compatibility

The matrix materials, Fe, Co and Ni, may be expected to react with SiC fibers to form their carbides or silicides at the interfaces. The possibility of the formation of these compounds can be determined using the thermodynamic data available in the literature as outlined below.

The carbides of both Co and Ni are unstable,⁽¹⁾ and therefore their formation by reaction between SiC and Co or Ni matrix can be ruled out. However, iron carbide (Fe_3C) is thermodynamically stable above about 800°C and its formation in an iron-matrix by the following interchange reaction may be expected:



The free energy change (ΔG) for this reaction is highly positive at fabrication temperatures proposed in this investigation. For example, at 1300°K, the free energy change (ΔG) is calculated to be about 14300 cal using the free energy of formation data for Fe_3C ⁽¹⁾ and SiC.⁽²⁾ Therefore, this reaction should also not occur during fabrication of SiC-superalloy composites.

During fabrication of superalloy composites with SiC fibers, the matrix materials (Fe, Co and Ni) may be expected to react with SiC to form various silicides by interchange reactions of the following type:



The standard heats of formation (ΔH°_{298}) for various silicides of Fe, Co and Ni are listed in Table 4. The free energies of formation (ΔG°_{298}) of these compounds can be assumed equal to their heats of formation (ΔH°_{298}) since the entropies for these solid intermetallic compounds are approximately equal to zero. Using the data in this table, the ΔC°_{298} (assumed equal to ΔH°_{298}) for reaction (2) is calculated to be -1700 cal. Since the free energy change is negative, reaction (2) can take place thermodynamically to form FeSi at the SiC-Fe (matrix) interface.

Similarly, the formation of all iron, cobalt and nickel silicides listed in Table 4, by reactions between the Fe, Co or Ni matrix and the SiC fibers, is thermodynamically predictable at the fabrication temperatures used in this investigation. The extent to which these reactions occur during fabrication depends on the interfacial kinetics and fabrication parameters such as temperature and pressure. Schneidmiller and White⁽⁶⁾ experimentally confirmed that SiC fibers react with Fe, Co and Ni matrices at temperatures above 800°C. The extent of the reaction increased in the order of Ni to Co to Fe. This is in conformity with the thermodynamic data listed in Table 4 which shows that the thermochemical stability increases and the melting point generally decreases in the order Fe, Co and Ni-silicides. The alloys investigated here are more complex and the predicted order of reactivity is not observed. Interferences from other phases may account for the reversal in reaction order. For example, Waspaloy contains 56 atomic percent Ni. However, 37% Ni is tied to Al and Ti in the form of γ' leaving 19% Ni in solution.

2.2.3 Diffusion Barrier Studies

Tungsten is the most obvious diffusion barrier candidate at this time because of its demonstrated effectiveness by the Watervliet Arsenal studies by I. Ahmad.⁽⁷⁾ However, a density penalty is incurred depending upon the barrier thickness required. Density calculations based on 50 v/o 0.0142 cm (0.0056 in.) dia. SiC (0.00127 cm (0.0005 in.) dia. W core) in a Hastelloy X matrix with various W barrier thicknesses are listed below:

<u>Thickness W-Coating-μm</u>	<u>50 v/o Composite Density g/cc</u>	<u>Density Penalty %</u>
0	5.69	0
2	6.0	5.5
5	6.27	10.3
10	7.35	29.3

From the above calculations we conclude that tungsten is a viable barrier material for this density limited application only if the required thickness is less than approximately 5 μm (10% penalty).

TABLE 4. STANDARD HEATS OF FORMATION (ΔH°_{298}) AND MELTING POINTS OF VARIOUS SILICIDES

<u>Compound</u>	<u>ΔH°_{298} (3,4) kcal/mole</u>	<u>Melting Point (3,5) $^{\circ}\text{C}$</u>
FeSi	- 19.2 \pm 1.5	1410
Co ₂ Si	- 27.6 \pm 2.0	1332
CoSi	- 24.0 \pm 2.0	1400
Ni ₃ Si	- 35.5 \pm 3.0	--
Ni ₂ Si	- 35.5 \pm 3.0	1318
NiSi	- 20.5 \pm 2.0	992
WSi ₂	- 22.2 \pm 3.5	--
SiC	- 17.5	--

The effectiveness of tungsten as a diffusion barrier between the three candidate alloys and SiC fibers was investigated. Tungsten coated, 0.004 in. dia. SiC fiber was received from Watervliet Arsenal via NASA-Lewis. Approximately 50 CVD* W coated fibers were loaded into 1/4" I.D. stainless capsules and filled with the three candidate alloys: Waspaloy, Hastelloy X, and Haynes Alloy 188. The capsules were evacuated and sealed by the usual procedure and HIP consolidated at 996°C (1825°F), 103 MPa (15,000 psi) with a 2 hour hold at temperature and pressure.

A metallographic analysis of as-HIP sections showed no interaction between the SiC fiber and the three candidate matrix alloys. A thin layer was observed on the tungsten-matrix interface for all three alloys. Sections of the three composites were heated for various times to 200 hours at 982°C (1800°F). Metallographic results of the 200 hour tests are shown in Figs. 16, 17 and 18 for Waspaloy, Hastelloy X, and HA-188 matrix composites. The porosity at the interface between the CVD W barrier and the matrix alloys Hastelloy X and Haynes-188 is due to Kirkendall void formation. The porous cylinder which surrounds each fiber can only degrade long time composite stability. No porosity could be observed on the Waspaloy-tungsten interface as shown in Fig. 16. Also of interest on Figs. 16-18 is the intermediate phase formation between tungsten and the matrix. Recent unpublished work on tungsten-Mar-M-200 composite has shown the intermediate phase in that system to be M_6C . The intermediate phase has yet to be identified in these systems. Regardless whether the phase is a carbide or intermetallic, interaction with the SiC fiber will commence when the tungsten barrier has been converted in-situ into the intermediate phase.

Interdiffusion between tungsten and matrix constituents which enter into the M_6C or other intermediate phase formation gives rise to Kirkendall void formation because of the large disparity in diffusion mobility between the coupled constituents. This phenomena

* CVD-chemical vapor deposited.

was evaluated by Jones⁽⁸⁾ as a function of solute addition to a Ni matrix. Void volumes at the tungsten wire interface was evaluated as a function of binary solute additions. Jones evaluated Ti, Al, V, W, Mo and Nb binary additions to the Ni matrix and plotted percent solute vs Kirkendall void volume at the interface of tungsten wire-binary solute couples heated for 100 hours at 1150°C (2100°F). The results are given in Figs. 19 and 20. Ti and Al binary additions showed minimum void volume values at 1% and 2% additions, respectively. It is perhaps not a coincidence that such additions are nearly totally consumed in the precipitation of γ' and are similar to the amounts commonly found in γ' strengthened superalloys such as Waspaloy.

The 982°C (1800°F) growth kinetics of the intermediate phase as shown in Fig. 21, are parabolic. A significantly lower growth rate constant is noted in the Ni base alloys than for the cobalt-based Haynes-188.

Intermediate phases between the SiC fiber and the .00127 cm (0.0005") dia. W core are revealed by Murikami's etch in Fig. 22. Strength degradation of the SiC fibers after exposure at high temperatures has been attributed to interaction between SiC and the tungsten core by I. Ahmad.⁽⁷⁾ The observation of this interaction at 982°C (1800°F) for times as low as 4 hours should indicate the possibility of reduced performance. Ultimately, carbon core fibers are preferred and should be considered for future work.

2.2.4 Matrix Alloy Selection

Pertinent properties on the three candidate alloys are listed in Table 5. On the bases of mechanical properties (principally ductility) and corrosion resistance alone, Hastelloy X or Haynes alloy 188 would be preferred with Hastelloy X being favored because of its lower density. However, the introduction of the tungsten diffusion barrier into the composite system forces us to consider the compatibility of the matrix alloy with tungsten rather than with SiC. The compatibility data presented above provides a compelling argument for the selection of a Waspaloy matrix alloy for the tungsten coated SiC fiber composite.

TABLE 5. PROPERTIES OF CANDIDATE MATRIX ALLOYS

Temp.	Coef.-Thermal Exp. in x 10 ⁻⁶ /in/ ^o F			0.2% YS ksi *			UTS ksi		
	HA-188	Hast. X	Wasp.	HA-188	Hast. X	Waspaloy	HA-188	Hast. X	Waspaloy
RT	6.39			69.5	52	115	139.4	114	185
200	6.59	7.7	6.8						
400	6.99	7.82	7.1						
600	7.40	7.90	7.4	48.5			116.3		
800	7.81	8.15	7.6						
1000	8.21	8.39	7.8	43.8	42	105	107.2	94	170
1200	8.68	8.56	8.0	43.9	40	100	103.1	83	162
1400	9.03	8.81	8.5	42.2	38	98	92.0	63	115
1600	9.44	9.02	8.9	38.0	26	75	60.7	37	76
1800	9.85	9.20	9.8	23.5	16	~ 40	36.8	22	~ 50
2000	10.25		10.4	11.5	8	~ 10	19.3	13	~ 20
2200				7.2			11.1		

Temp.	Modulus psi x 10 ⁶			Elong. %		
	HA-188	Hast. X	Waspaloy	HA-188	Hast. X	Waspaloy
RT	33.6	28.6	30.9	56	43	25
200	32.8	28.1	30.4			
400	31.5	26.9	29.5			
600	30.2	25.8	28.6	71		
800	28.9	24.6	27.7			
1000	27.6	23.4	26.7	70	45	23
1200	26.2	22.3	25.6	61	37	34
1400	24.9	21.1	24.3	43	37	28
1600	23.6	19.9	22.9	73	50	35
1800	22.3	18.5	21.1	72	45	
2000	21.0			47	40	
2200				35		
Density	Waspaloy		0.296 lb/in ³ (8.19 gm/cm ³)			
	Hastelloy X		0.297 lb/in ³ (8.22 gm/cm ³)			
	Haynes-188		0.330 lb/in ³ (9.13 gm/cm ³)			

* 1 psi = 6.895 x 10⁻³ MPa

3. COMPONENT CHARACTERIZATION

3.1 Matrix Mechanical Properties

Mechanical properties evaluation was conducted on both Hastelloy X and Waspaloy while other work was in progress to select the optimum matrix from compatibility considerations.

The matrix chosen for compositing was in the form of powder that had been formed into a powder tape by use of a fugitive binder. Mechanical test specimens were machined from hot isostatically pressed powder material from the same lot of material that was made into powder tape. Properties were evaluated for materials that were HIP consolidated at 1038°C (1900°F) and 996°C (1825°F) at 103 MPa (15 ksi) for two hours.

Mechanical testing was conducted on 0.18 in. diameter specimens with a one-inch gauge length and threaded grips. Temperature was controlled to $\pm 1^\circ\text{C}$ in the high temperature tests by a solid state controller. The strain rate was 0.05 min.

The resulting data are compared to INCO values in Table 6 for the 1038°C HIP material and plotted vs test temperature in Figs. 23 and 24. The 996°C HIP tensile properties are compared to 1038°C HIP tensile properties in Table 7. The Waspaloy alloy which was chosen as the composite matrix alloy displays superplastic behavior at 982°C (1800°F) with over 200% elongation. However, much surface void formation was noted. A metallographic examination of the Waspaloy tensile specimens after tensile testing at 871°C (1600°F) and 982°C (1800°F) in Figs. 25 and 26 show normal uniform elongation at 871°C but massive grain boundary separation at 982°C. The superplastic behavior is limited to the precipitation hardened Waspaloy powder metallurgy alloy because grain growth does not occur during the HIP consolidation process. Hastelloy X, being a solid solution alloy does experience grain growth beyond the prior powder boundaries during HIP consolidation. This grain growth precludes any superplastic behavior.

TABLE 6. PROPERTIES OF CANDIDATE MATRIX ALLOYS

<u>Coef.-Thermal Exp. in x 10⁻⁶/in./°F</u>		<u>0.2% YS ksi***</u>		<u>UTS ksi</u>	
<u>Temp.</u>	<u>Hast. X*</u>	<u>Wasp.</u>	<u>Hast. X</u>	<u>Waspaloy</u>	<u>Hast. X</u>
RT			52 (61.7)**	115 (138.3)	114 (116.0)
200	7.7	6.8			
400	7.82	7.1	(49.5)	(124.9)	(102.2)
600	7.90	7.4			
800	8.15	7.6	(43.7)	(121.4)	(96.1)
1000	8.39	7.8	42 (41.0)	105 (119.4)	94 (93.3)
1200	8.56	8.0	40	100 (114.0)	83
1400	8.81	8.5	38 (36.9)	98 (111.0)	63 (56.1)
1600	9.02	8.9	26 (32.5)	75 (53.1)	37 (34.6)
1800	9.20	9.8	16 (17.6)	~40 (18.0)	22 (17.7)
2000		10.4	8	~10	13
2200					~20
<u>Modulus psi x 10⁶</u>		<u>Elong. %</u>		<u>Reduction in Area %</u>	
<u>Temp.</u>	<u>Hast. X</u>	<u>Waspaloy</u>	<u>Hast. X</u>	<u>Waspaloy</u>	<u>Hast. X</u>
RT	28.6	30.9	45 (41.6)	25 (26.5)	(40.8)
200	28.1	30.4			(38.3)
400	26.9	29.5	(42.8)	(24.0)	(37.1)
600	25.8	28.6			(29.3)
800	24.6	27.7	(44.2)	(22.8)	(42.0)
1000	23.4	26.7	45 (42.2)	23 (21.4)	(40.8)
1200	22.3	25.6	37	34 (23.0)	(19.6)
1400	21.1	24.3	37 (27.8)	28 (15.8)	(21.0)
1600	19.9	22.9	50 (22.8)	35 (12.4)	(23.8)
1800	18.5	21.1	45 (8.8)	(211.0)	(15.2)
2000	21.0		40		(12.3)
2200					(4.7)
<u>Density</u>	<u>Waspaloy</u>		0.296 lb/in ³ (8.19 gm/cm ³)		
	<u>Hastelloy X</u>		0.297 lb/in ³ (8.22 gm/cm ³)		
	<u>Haynes-188</u>		0.330 lb/in ³ (9.13 gm/cm ³)		

* Data from Nickel Base Alloys, International Nickel Co., 1964.

** Brackets (61.7) denote values for Waspaloy and Hast. X measured during this investigation - strain rate = 0.05 in/in/min.

*** 1 psi = 6.805 x 10⁻³ MPa

Table 7

Test Temp./HIP Temp.	2% YS-ksi*				UTS-ksi				Ductility			
	Hast. X		Waspaloy		Hast. X		Waspaloy		Hast. X		Waspaloy	
	1900°F	1825°F	1900°F	1825°F	1900°F	1825°F	1900°F	1825°F	1900°F	1825°F	1900°F	1825°F
RT	61.7	85.6	138.3	155.6	116.0	132.4	196.4	204.1	41.6	22	21.5	18
1600°F	32.5	36.1	53.1	40.1	34.6	39.5	54.7	54.0	(40.8)	(25)	(38.3)	(26)
1800°F	17.6	14.8	18.0	12.8	17.7	16.8	18.9	18.9	(15.2)	(10.8)	(12.3)	(1.6)

$$1 \text{ psi} = 6.895 \times 10^{-3} \text{ MPa}$$

3.2 Tensile Strength of SiC filament

Tensile properties of SiC filament used in this study were characterized at room temperature and 982°C (1800°F). Pneumatic grips lined with a double layer thickness of heavy duty aluminum broiler foil were used for both high and low temperature tensile tests. The gauge length was one inch for low temperature tests. The total length of filament evaluated for the elevated temperature tests was 16 in. per test. However, the 982°C (1800°F) tests were conducted in an inert gas tube furnace with approximately a one inch uniform hot zone. The time at temperature prior to testing was two minutes. A flowing 90% N₂-10% H₂ (forming gas) atmosphere was provided for the high temperature because of the need for protecting the CVD tungsten barrier from oxidation. This atmosphere was also provided for the uncoated filaments. Companion tests on uncoated filaments were conducted with flowing argon and static air atmospheres with no significant change in tensile strength (average of 10 tests).

The tensile data for RT and 982°C test temperatures are summarized in Table 8. Also given in Table 8 are high, low, average, and standard deviation values. Ten tests were conducted for each material temperature. Of particular interest are the three filament lots supplied by Watervliet Arsenal with a CVD tungsten diffusion barrier. The loss of room temperature strength during the CVD process was approximately 138 MPa (30 ksi) out of 2965-3310 MPa (430-480 ksi) average prior to coating. This strength decrement is considered to be insignificant. The 982°C (1800°F) strength of Lot 8S69 (the only lot tested prior to coating) showed a greater strength and lower standard deviation for the coated material.

Micrographs of the as-coated material in Fig. 27 show the coating to be irregular for Lots 8S69 and 8S80 but quite uniform for S-662. The as-coating thickness for each lot is given below:

<u>Lot</u>	<u>CVD-W Thickness - μm</u>
8S80	3-5
8S662	6-8
8S69	3-5

TABLE 8. STRENGTH OF SiC FILAMENT

<u>Spool #</u>	<u>Dia. mil</u>	<u>ksi*</u>	<u>High</u>	<u>Low</u>	<u>Ave</u>	<u>Std Dev</u>	<u>σ</u>
<u>RT</u>							
8S69	5.64**	483	367	446	47.0	W core CVD W coated (430 prior to CVD)	
8S80	5.6**	492	367	414	47.0	W core CVD W (440 ksi prior to CVD)	
S662	5.6**	515	335	434	60.0	W core CVD W coated (480 ksi prior to CVD)	
8S43	5.71	481	362	438	34.0	W core	
8S103	5.6	521	348	462	78.2	W core	
8S104	5.6	524	430	493	30.6	W core	
1S71	5.6	851	712	812	41.0	Carbon core	
<u>1800°F</u>							
8S69	5.64*	308	269	294	16.0	W core CVD W coated	
S662	5.6*	357	268	296	35.0	W core CVD W coated	
8S80	5.6*	357	330	343	8.0	W core CVD W coated	
8S43	5.71	224	175	205	20.0	W core	
1S71	5.6	313	197	264	38.0	Carbon core	
8S65	5.68	255	139	190	38.0	W core	
8S64	5.52	215	161	195	48.0	W core	
8S69	5.64	322	237	271	24.0	W core	
8S106	5.6	229	175	197	23.0	W core	
8S100	5.6	153	224	205	23.0	W core	
8S105	5.6			128		W core	
8S97	5.6	125	179	142	24.0	W core	
8S96	5.6	161	210	180	21.0	W core	
8S98	5.6	165	251	208	21.0	W core	
8S99	5.6	137	184	168	18.0	W core	
8S102	5.6	139	188	160	19.2	W core	
8S108	5.55	201	116	169	30.0	W core	
8S75	5.6	214	152	165	20.0	W core	
8S49	5.6	215	175	187	14.0	W core	
8S42	5.6	170	125	154	15.0	W core	

* 1 ksi - 6.895 MPa

** Dia. of uncoated filament

4. COMPOSITE FABRICATION

4.1 Composite Design

The basic composite design for uniaxial arrays is shown schematically in Fig. 28. The center to center fiber spacing (ℓ_R) for a triangular array is

$$\begin{aligned}\ell_R &= \sqrt{\frac{\pi}{2\sqrt{3}}} \cdot D_R \left(\frac{1}{f}\right)^{1/2} \\ &= 0.952 D_R \left(\frac{1}{f}\right)^{1/2}\end{aligned}$$

The foil thickness is given by

$$\begin{aligned}T_m &= \ell_R \frac{\sqrt{3}}{2} (1-f) \\ &= 0.866 \ell_R (1-f)\end{aligned}$$

where T_m = matrix foil thickness

D_R = fiber diameter

f = volume fraction of fiber in composite.

When powder tape is used, T_m must be divided by the tap density of the tape expressed as a fraction of theoretical density (approximately 0.5).

With 0.0142 cm (0.0056 in) dia. fibers and a volume fraction of 0.5

$$\ell_R = 0.0192 \text{ cm (0.00754 in.)}$$

$$T_m = 0.0083 \text{ cm (0.00326 in.) (foil) or}$$

$$\sim 0.0165 \text{ cm (0.0065 in.) (powder tape)}$$

Likewise for 25 volume fraction composite

$$\ell_R = 0.0272 \text{ cm (0.0107 in.)}$$

$$T_m = 0.0175 \text{ cm (0.0069 in.) (foil) or } 0.0353 \text{ cm (0.0139 in.) (powder tape)}$$

The above calculations guided the composite fabrication.

4.2 Binder Removal

An important aspect of the composite fabrication sequence is removal of the binder from the powder tape. The binder in the tape from the Vita Corporation is polymethyl methacrylate (PMMA). Thermogravimetric analysis performed on tape heated at 5°C/min in-vacuo showed that all of the binder was removed after heating to 435°C (815°F).

A capsule was filled with Vita-tape (Mar-M-200 powder) and heated for four hours at 400°C under a roughing vacuum. The tube was then cooled and transferred to the encapsulation rig and heated to 500°C under evacuation and sealed.

This particular capsule was HIPed at 1205°C (2200°F) for 2 hours at 103.4 MPa (15,000 psi). The resulting microstructure as revealed by SEM is shown in Fig. 29. The light precipitates are carbides. A HIP compact utilizing powder from the same lot is shown in Fig. 30. Although there is some difference in thermal history between the specimens of Fig. 29 and 30, the distribution or density of carbides is very similar. We conclude that binder removal will not be a serious problem as long as the composite is outgassed for a sufficient time and temperature prior to sealing.

4.3 Composite Panel Fabrication

Several attempts at applying fibers to foil matrix materials were made, all resulting in failure due to our inability to maintain fiber alignment. The matrix foil approach works with aluminum matrix composites because the room temperature softness of aluminum allows the fibers to become imbedded into the foil with a modest amount of pressure, thus fixing their position. Waspaloy foil, after rolling to 0.0820 cm (0.00325 in.) thickness is extremely hard. This hardness cannot be sufficiently reduced by heat treating due to the profuse γ' precipitation. On the other hand, the use of powder alloy/polymer tape has proven to be quite successful and has been chosen for all future composite panel development.

Mandrel winding using a standard machine lathe is employed to lay the fibers onto the powder tape. A fixture was constructed for placement on the tool post bed which holds the reel and tensions the fiber. The 0.0127 cm (0.0050 in.) thick tape made by Vita Corp. from -325 mesh argon atomized Waspaloy powder is layed onto the 8 in. diameter mandrel. The filament is uniformly wound onto the powder tape by simultaneously rotating the mandrel and axially translating the tool post bed at a fixed rate of 0.0178 cm (0.007 in.) per revolution. Alternate layers of tape and fiber monolayers are built up to achieve the proper number of unidirectional plies. Proper lengths are obtained by transverse cuts across ply with a diamond cutting wheel attached to a hand-held grinder.

Angle ply lay ups are produced similarly except that the SiC filaments are wound onto a Mylar sheet. After winding the array is sprayed with an acrylic lacquer to allow the filament to be handled in the form of a fiber monolayer. Winding irregularities do occur as shown in Fig. 31a, will be eliminated with the design of a more rigid feed, and tensioning device and more uniform drive. The filament monolayers are cut by guillotine shearing and stacked into the desired array with powder tape (Fig. 31b).

The next step in the procedure involves canning for subsequent hot isostatic pressing. Several canning materials can be utilized depending upon requirements. Low temperature tensile specimens are fabricated from composites pressed in 304 stainless steel picture frame cans. Elevated temperature specimens have been canned in Waspaloy. Finally, mild or aluminum killed steels are used for fabrication of demonstration panels. In this case, the canning material will be leached away.

In all cases, regardless of the canning material, a picture frame is made having its interior geometry the same as the desired composite and is joined by spot welding. After press fitting the green composite into a picture frame with a spot welded bottom cover plate in place, the "Open Face Sandwich" is heated in forming gas (90% N₂-10% H₂) to a temperature of 400°C(750°F) at a rage of 28°C(50°F) per hour to evolve the

polymer binder. The top cover plate is then spot welded to the picture frame and the entire periphery is TIG welded. Spot welding has lead to failures in some of our earlier composite specimens and panel attempts because of a tendency to blast pinhole leaks through the cover plate. These problems have been overcome by double encapsulation with an outer mild steel leachable can. Final evacuation is accomplished by electron beam filling of a small hole drilled through the envelope.

After leak testing, the assembly is HIP (hot isostatically pressed) at 995-1038°C (1825 to 1900°F) for two hours at 138 MPa (20 ksi) (138 MPa). The composite package is kept flat by clamping between thick steel plates during the HIP operation.

After solving the envelope leakage problems, a tensile specimen blank was successfully consolidated at a 1038°C (1900°F) HIP temperature. However, there remained two problems to be overcome in the fabrication sequence:

- (1) Insufficient barrier protection during HIP operation, resulting in matrix embrittlement.
- (2) Use of excessively heavy gauge HIP envelope results in excessive residual thermal stresses.

These two factors combined to produce the delamination upon longitudinal sectioning during specimen fabrication shown in Fig. 32.

A metallographic transverse composite photograph is shown in Fig. 33. This panel was four layers thick. Breakdown of the barrier resulting in chemical interaction is apparent in this photomicrograph and in Figs. 34 and 35. The cracks noted in Fig. 33 exposed longitudinal sections on the fracture face as shown in Fig. 36.

The volume fraction SiC within the fiber bundle at the upper right corner of Fig. 33 was measured as 54%, confirming the earlier calculations based on 60% of theoretical density of the powder alloy tape.

The compatibility problem and thermal stress problems that lead to the delamination noted above have been solved or alleviated by utilizing thinner encapsulation material and by hot isostatic pressing at a somewhat lower temperature, 996°C (1825°F). The thicker CVD tungsten coated material is being used for all future test specimens. Two composite test specimens were consolidated utilizing a thin gauge 0.083 cm (0.032 in.) mild steel envelope. The resulting compact and a test specimen machined from the compact is shown in Fig. 37.

The lessons learned from the above compositing efforts can be summarized into the following admonitions:

(1) The HIP envelope must be sufficiently thin to avoid cooling stresses resulting from differential thermal expansion between the composite section and the envelope material.

(2) Thermal stresses should be further reduced by utilizing a leachable HIP envelope such as low carbon steel. Aluminum killed steel was selected because of its weldability.

(3) Sharp edges on the composite bundle or picture frame must be avoided because of a hot tearing tendency in mild or aluminum killed steel during HIP consolidation while the envelope is deforming to conform to the picture frame. Hot tearing results in leaks in the can and a loss of pressure differential required for consolidation.

(4) Thermal stresses can be further reduced by plasma spraying the inside of the envelope with zirconia. The zirconia prevents bonding between the composite bundle and the envelope.

5. MECHANICAL PROPERTY EVALUATION

The original scope and work plan for this program includes a considerable amount of tensile testing of low and high volume fraction composites in longitudinal, transverse, and angle ply configurations after varying degrees of thermal exposure and thermal cycling, at both

room temperature and 982°C (1800°F). However, the demonstrated necessity for a diffusion barrier between the SiC filament and the matrix alloy and the time delays in procuring a sufficient amount of tungsten coated filament to get on with the fabrication development precluded completion of the mechanical property evaluation. However, this work is progressing under the present contract (NAS3-19735). Nevertheless, one specimen was fabricated and tested revealing much useful information.

A composite tensile specimen was fabricated in order to evaluate the high temperature composite test specimen design shown in Figs. 37 and 38. This specimen was HIP at 995°C (1825°F), 138 MPa (20 ksi). The fiber was from lot 8S80 which was imperfectly CVD coated. Tensile testing was conducted at 982°C (1800°F) at a strain rate of 0.05/min. The stress-strain curve of Fig. 39 shows moderate strengthening due to the presence of the reinforcement and ductility of 5% which is a large amount for composites. Although the volume fraction within the fiber bundle was 54%, the overall volume fraction was considerably less due to the excessively thick cladding. The ultimate overall strength was 152 MPa (22 ksi). By application of the rule of mixtures and the knowledge of the HIP matrix strength, a fiber strength of 917 MPa (133 ksi) was calculated.

A radiographic enlargement of the guage section in Fig. 40 revealed extensive cracking and fiber breakage. Although the fiber strength in the composite was less than half of the as-coated fiber, the extensive cracking and high ductility indicates that effective load redistribution accompanied the fiber breakage.

An SEM examination of the fracture surface in Fig. 41 shows only a moderate amount of fiber pull-out (~ 1 fiber diameter). The fiber fracture in most cases originates at the surface. Closer examination reveals discrete areas of chemical interaction at the origin of many of the fiber fractures. These defects are presumed to be due to thin spots or defects in the CVD W coating.

6. DISCUSSION OF RESULTS

This investigation has demonstrated that useful composites of silicon carbide filament/superalloy class are impossible unless the filament is first coated with a diffusion barrier or more properly, a diffusion retardant. Tungsten, applied by CVD techniques, was shown to be a viable coating on the SiC filament within the limits to be discussed here.

The stated application of composite material developed during this investigation is for exhaust system components. The driving force behind the investigation is the possibility of a 1/3 weight reduction due to the low density of SiC. The use of tungsten as a barrier material between the SiC and matrix results in an increase in density of the composite. The tungsten barrier thickness should be minimized for density or weight sensitive applications. However, we see from Fig. 21 that tungsten prevents interaction between the matrix and filament by itself interacting with matrix constituents and producing in-situ an intermediate phase. With extensive conversion of the tungsten layer into intermetallic phases, inevitable contact and interaction between SiC and the intermetallics occur, which result in the formation of complex silicides and carbides. The useful composite life is thus determined by the kinetics of growth of the intermediate phase. By reference to Fig. 21 we see that if we wish 1000 hr life, we must have an 8 μm initial coating thickness and a 18 μm coating thickness for a 5000 hr life (neglecting the volume change with phase formation). These coating thicknesses would result in a density of 7.2 gm/cc and 8.6 gm/cc, respectively for a 50 v/o composite. These densities are compared to the Waspaloy matrix density of 8.2 gm/cc. The density advantage of SiC/superalloy composites is lost with excessively thick tungsten barriers.

Nevertheless, other barrier coatings are possible, i.e., carbides and nitrides of Ti, Zr and Hf, which would result in lesser density penalties or in the case of Ti and Zr carbides and nitrides, density improvements. These coatings must be developed before SiC/superalloy composites can be

used for this stated application. This statement does not imply that current work on presently available tungsten coated fibers are not useful. On the contrary, we can learn all of the required lessons in fabrication and short term mechanical properties utilizing tungsten coated filament in the Waspaloy matrix. It is only in the final application that we must have a less dense and more protective diffusion barrier.

This later task will be addressed and better defined in the continuation work now in progress under Contract NAS3-19735.

7. SUMMARY OF RESULTS

The potential of SiC/superalloy composites was verified if adequate diffusion barrier protection between matrix and filament is provided. The results of this program can be summarized as follows:

- (1) Room temperature filament strengths of 2758 to 3448 MPa (400 to 500 ksi) were measured. The strength degraded by no more than 276 MPa (40 ksi) after subsequent CVD W barrier coating.
- (2) The 982°C (1800°F) filament strength varied greatly from lot to lot with values of 883 to 6088 MPa (128 to 345 ksi) measured. The CVD W coated material was stronger with values of 2027 to 6088 MPa (294 to 343 ksi).
- (3) Unprotected SiC filament reacted with all of the matrix candidates to an unacceptable extent. The reaction was least severe with Waspaloy, HA-188 and Hastelloy X compositions.
- (4) A CVD layer of tungsten on the filament provides adequate short time protection (< 1000 hrs) without unduly increasing the composite density.
- (5) Kirkendall void formation at the tungsten interface between the CVD tungsten and matrix was used as a criteria for eliminating HA-188 and Hastelloy X from further consideration. Waspaloy was chosen as the

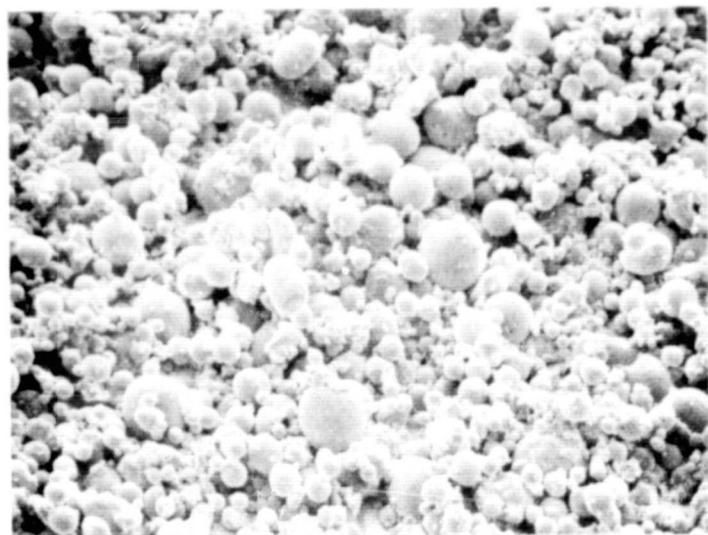
scale-up matrix alloy because of the absence of Kirkendall voids and the low parabolic growth rate constant for the intermetallic phase between tungsten and matrix constituents.

(6) The SiC filaments in the Waspaloy matrix degrade when the CVD W layer has been consumed in intermetallic phase formation. Filament strengths of 918 MPa (133 ksi) were measured at 1800°F in a 50 v/o composite.

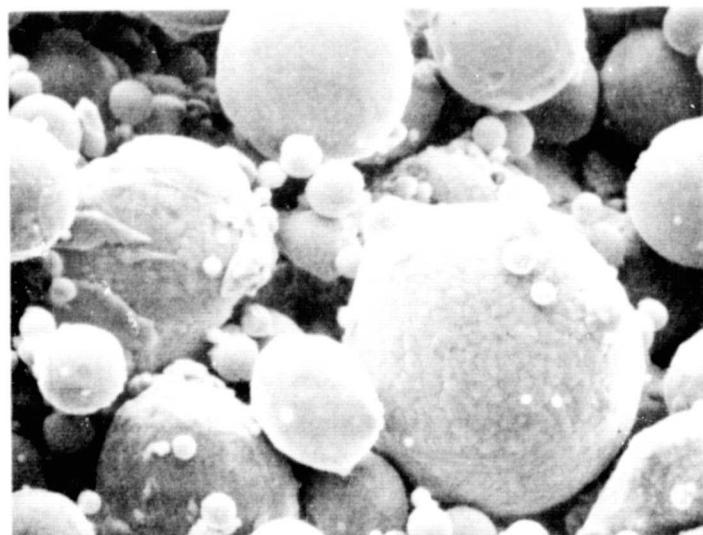
(7) Fabrication techniques were developed for producing small panels and specimens at the 50 v/o level by utilizing the matrix in the form of powder tape with a fugitive binder and consolidation by hot isostatic pressing at temperatures as low as 996°C (1825°F).

8. REFERENCES

1. F. D. Richardson, "The Thermodynamics of Metallurgical Carbides and Carbon in Iron", J. Iron and Steel Inst., 175, (1953), 33.
2. D. R. Stull and H. Prophet, et al., "JANAF Thermochemical Tables", NSRDS-NBS 37, (1971).
3. O. Kubaschewski, E. LI. Evans and C. B. Alcock, "Metallurgical Thermochemistry", Pergamon Press, (1967).
4. O. Kubaschewski and J. A. Catterall, "Thermochemical Data of Alloys", Pergamon Press, (1956).
5. M. Hansen, "Constitution of Binary Alloys", McGraw-Hill Book Co., Inc., (1958).
6. R. F. Schneidmiller and J. E. White, "A Comparability Study of SiC and B. Fibers", in Advanced Fibrous Reinforced Composites, SAMPE, Vol. 10, (1966), p. E-53.
7. I. Ahmad, private communication.
8. R. Jones, unpublished investigation.



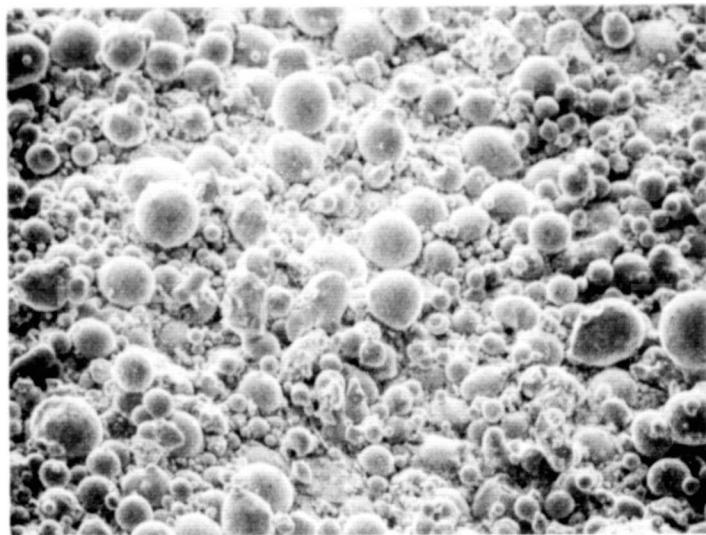
200 X



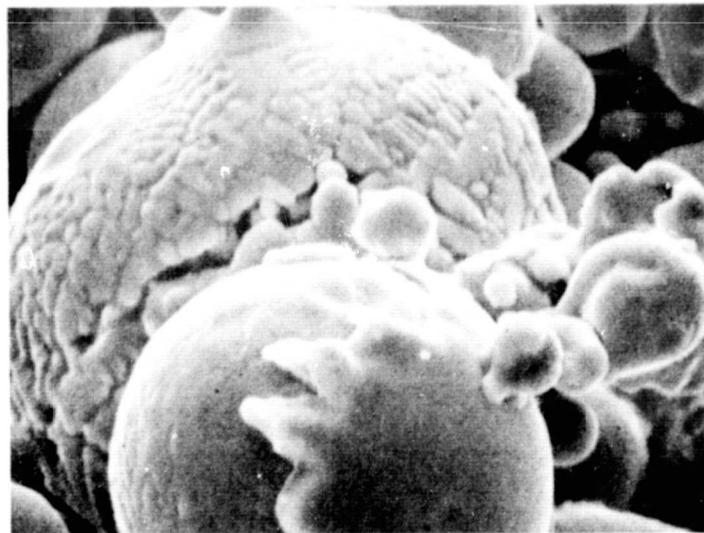
1000X

FIG. 1 -- SEM PHOTOGRAPHS OF AS-RECEIVED (-325 MESH) WASPALOY POWDER
HEAT NO. L-180 (KELSEY-HAYES)

REPRODUCIBILITY OF THE
ORIGINAL PAGE IS POOR



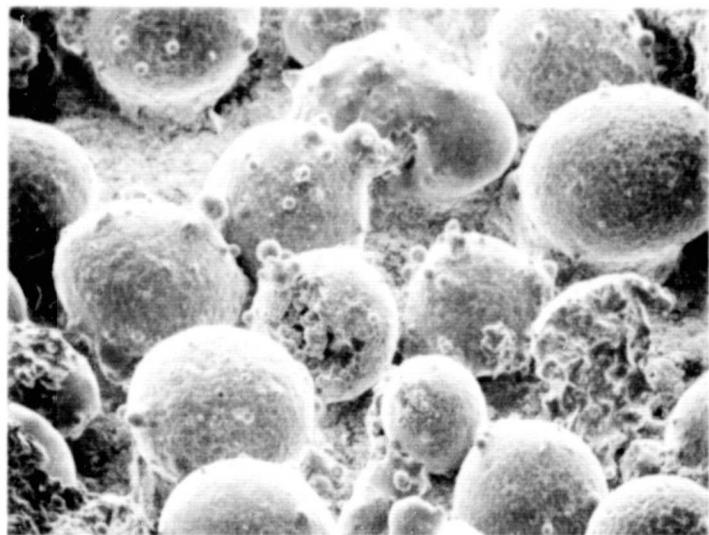
200 X



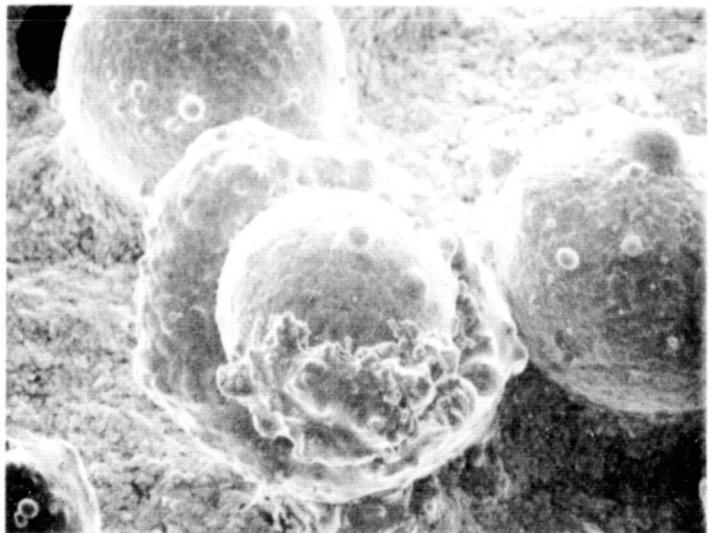
2000X

FIG. 2 -- SEM PHOTOGRAPHS OF -325 MESH FRACTION OF HASTELLOY X POWDER
HEAT NO. 6080 (ALLOY METALS, INC.)

REPRODUCTION OF THIS PAGE
ORIGINAL PAGE IS POOR



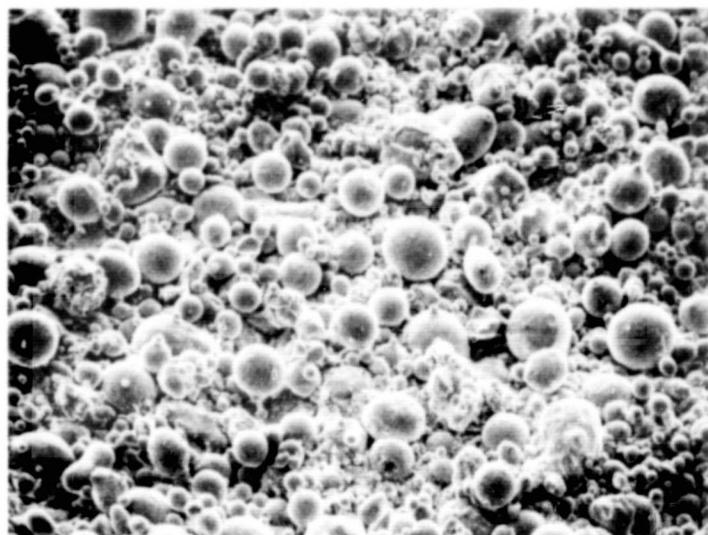
100 X



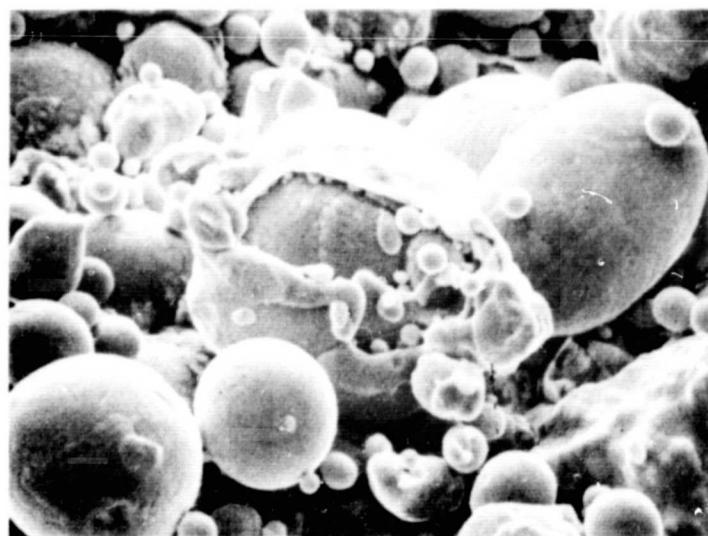
200 X

FIG. 3 -- SEM PHOTOGRAPHS OF AS-RECEIVED (-60 + 100 MESH) NiCrAlY POWDER
HEAT NO. L-43 (KELSEY-HAYES)

REPRODUCIBILITY OF THE
ORIGINAL PAGE IS POOR



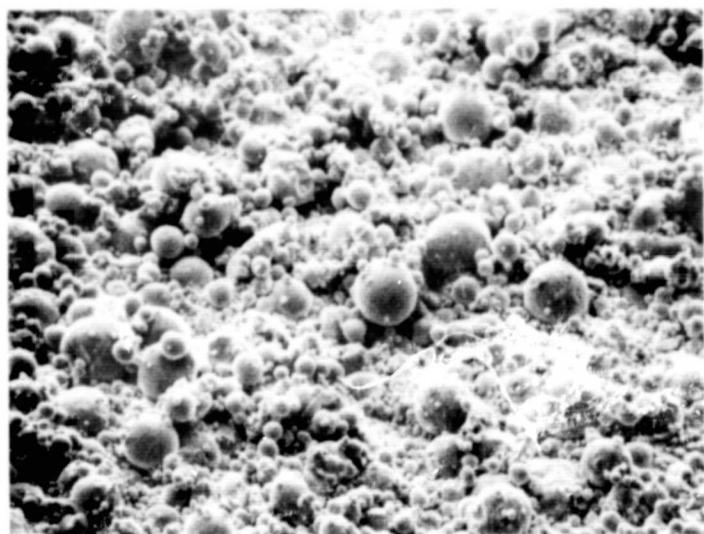
200 X



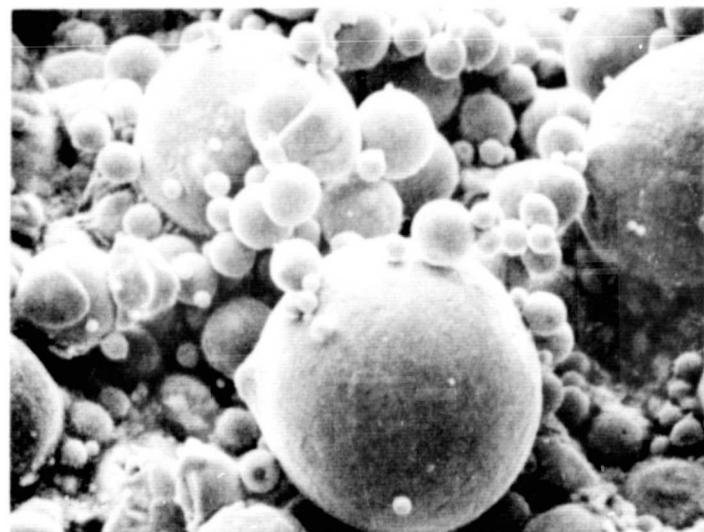
1000 X

FIG. 4 -- SEM PHOTOGRAPHS OF -325 MESH FRACTION OF HAYNES 188 POWDER
HEAT NO. 6083 (ALLOY METALS, INC.)

REPRODUCIBILITY OF THE
ORIGINAL PAGE IS POOR

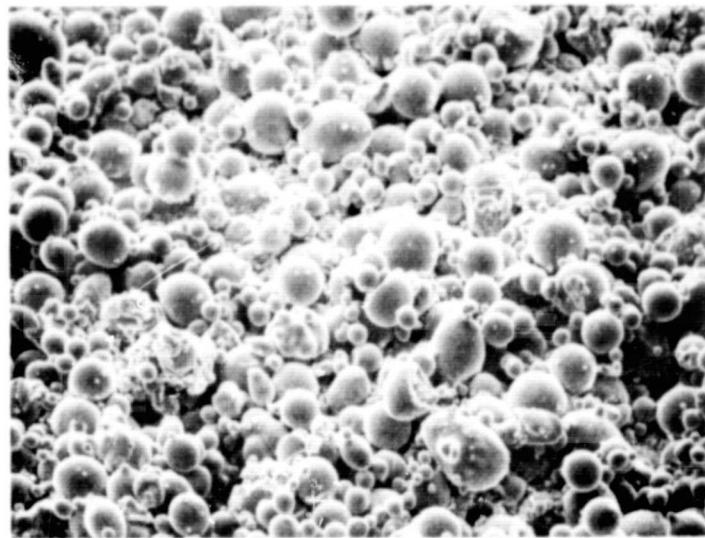


200 X

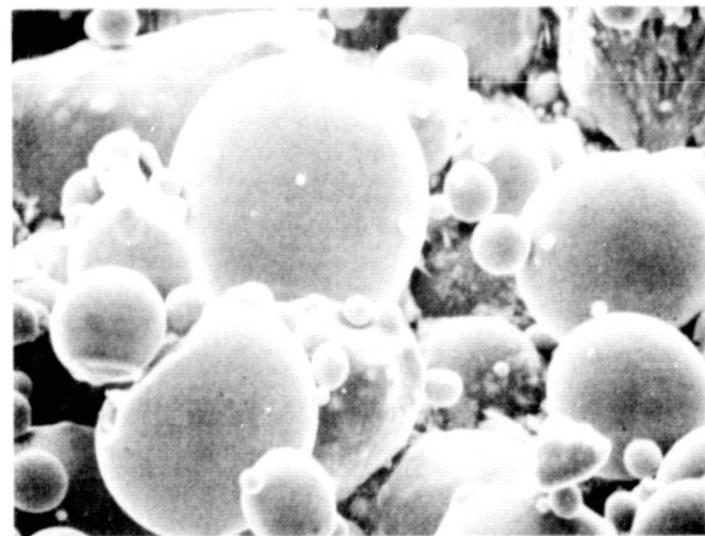


1000 X

FIG. 5 -- SEM PHOTOGRAPHS OF -325 FRACTION OF ALLOY S-57 POWDER HEAT NO. 6153 (ALLOY METALS, INC.)

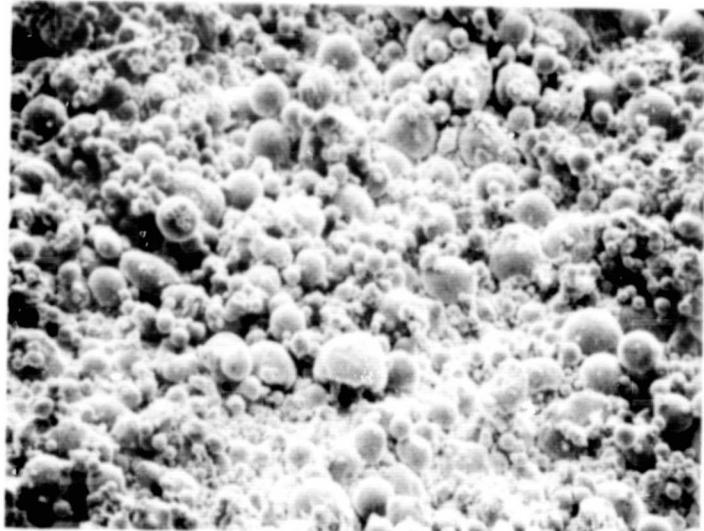


200 X

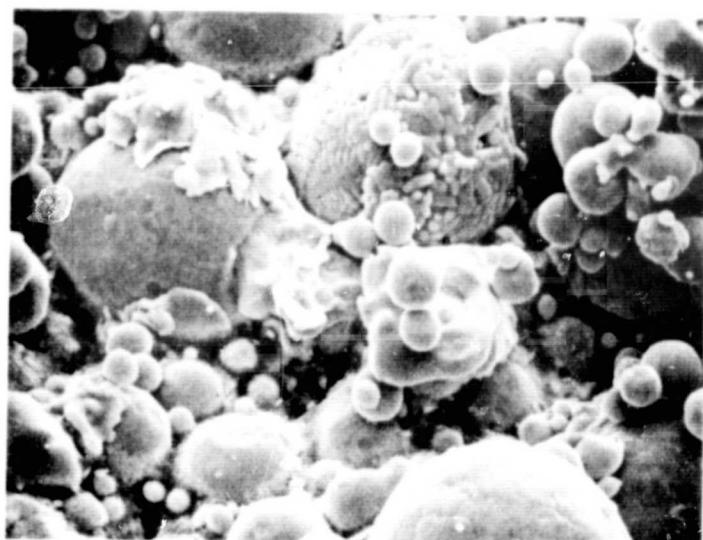


1000 X

FIG. 6 -- SEM PHOTOGRAPHS OF AS-RECEIVED FeCrAlY POWDER HEAT NO. L-170
(KELSEY-HAYES)

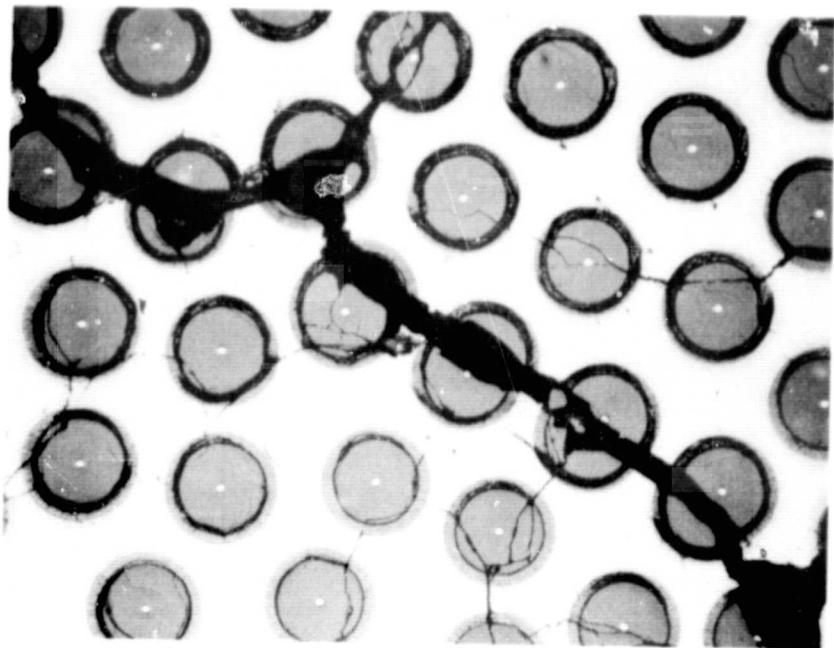


100 X

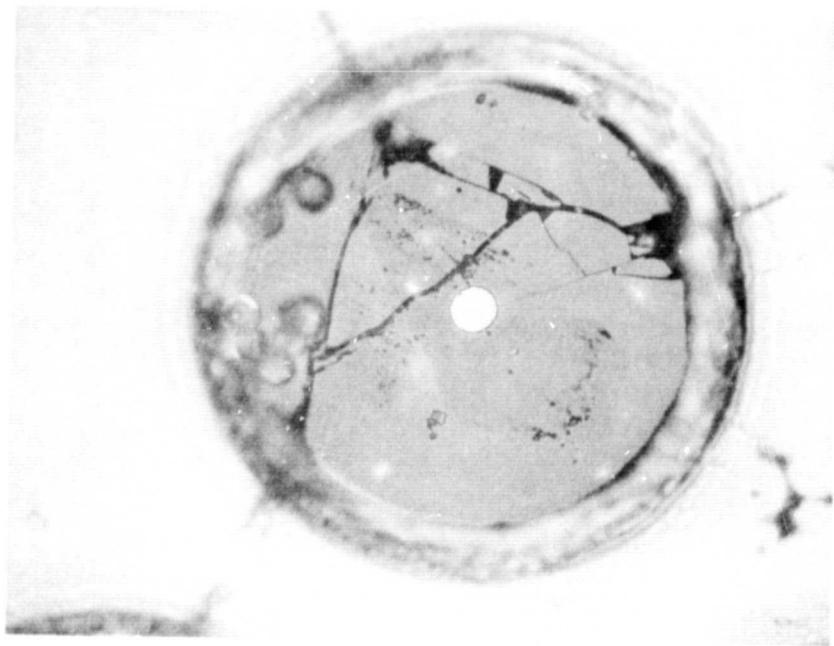


1000 X

FIG. 7 -- SEM PHOTOGRAPHS OF -325 MESH FRACTION OF INCOLOY 800 POWDER
HEAT NO. 6153 (ALLOY METALS, INC.)



100 X



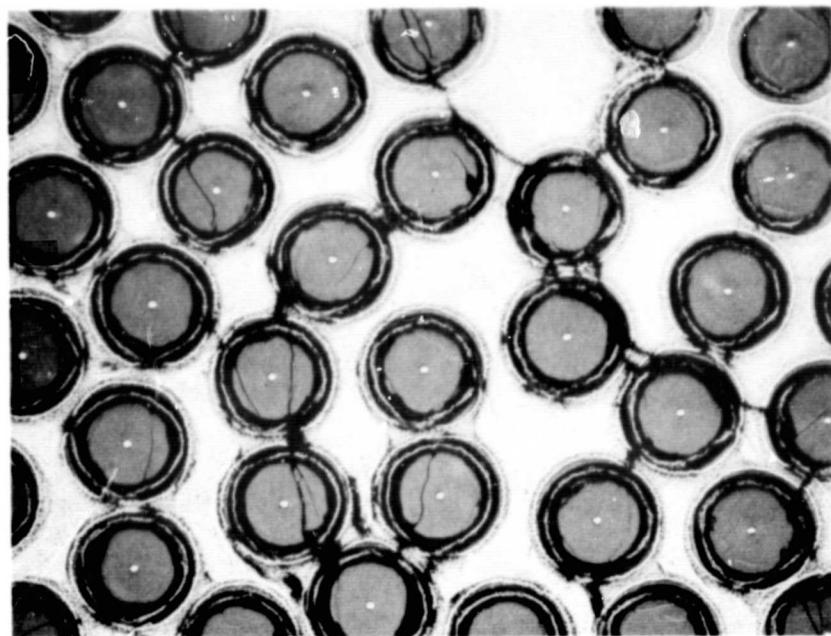
500 X

N-2438

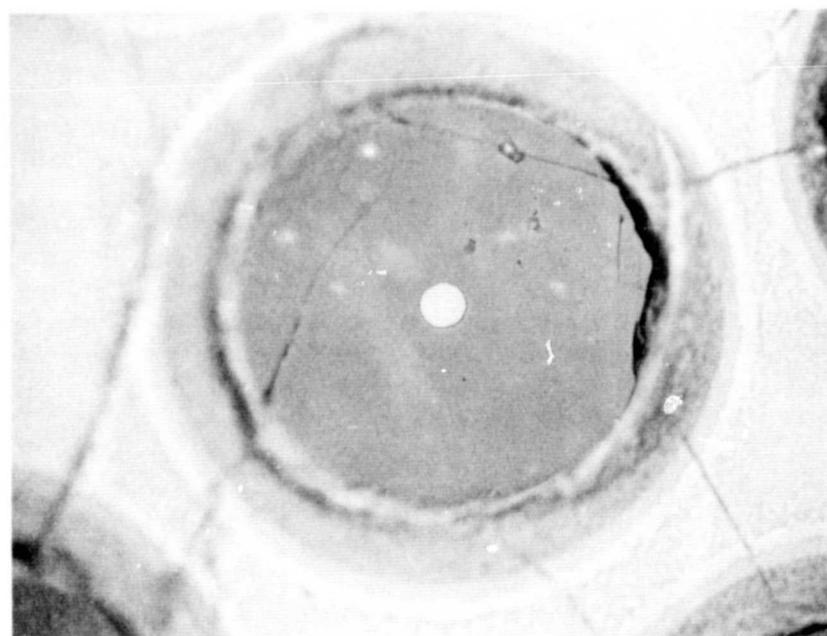
FIG. 8 -- Microstructure of SiC/Haynes-188 composite after HIP
2 hours at 1825°F (996°C), 15,000 psi

REPRODUCIBILITY
ORIGINATOR

RM-62409



100 X

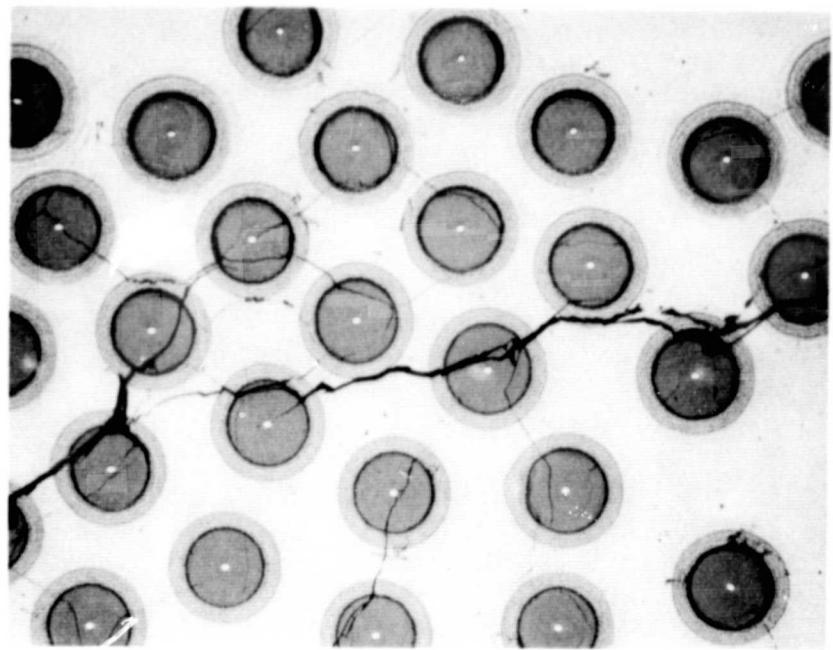


500 X

N-2441

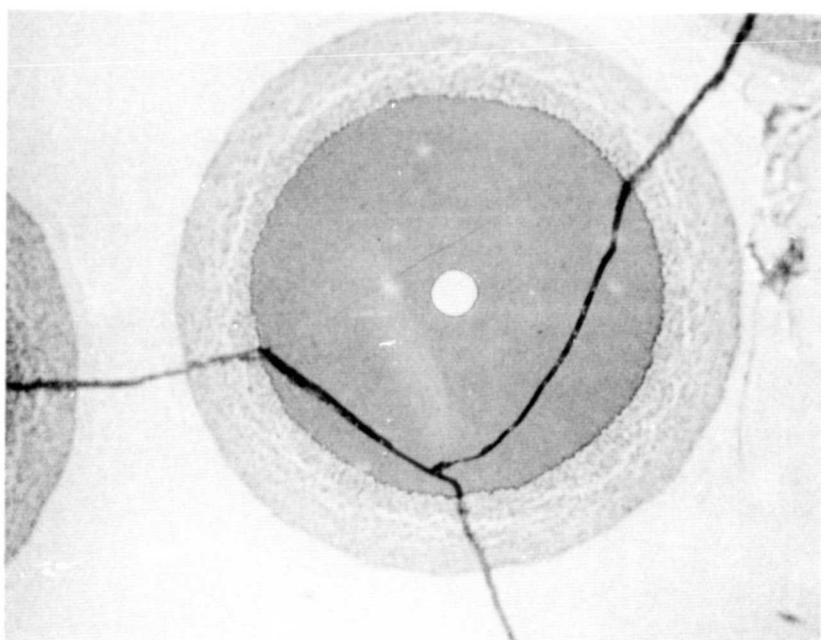
FIG. 9 -- Microstructure of SiC/Waspaloy composite after HIP 2 hours
at 1825°F (996°C), 15,000 psi

RM-62410



A)

100 X

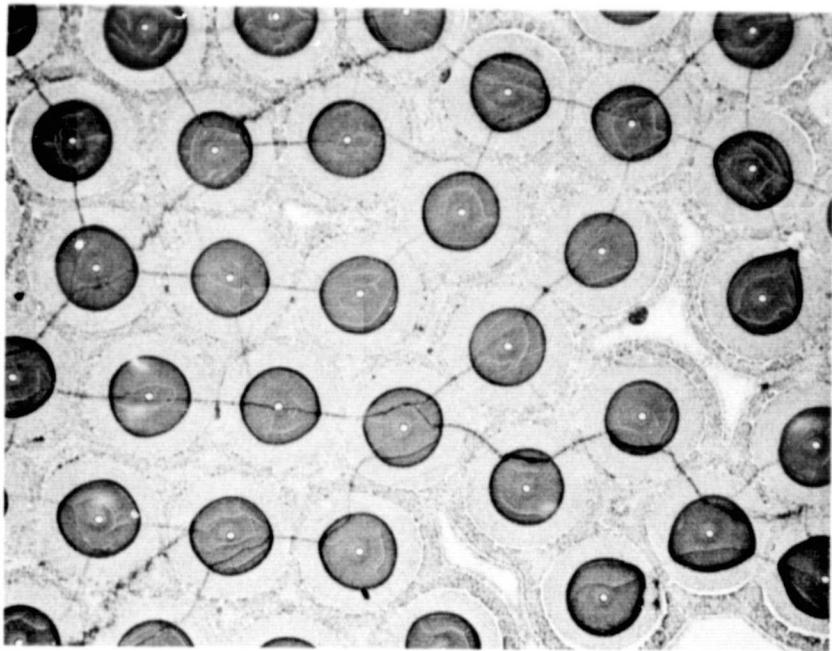


B)

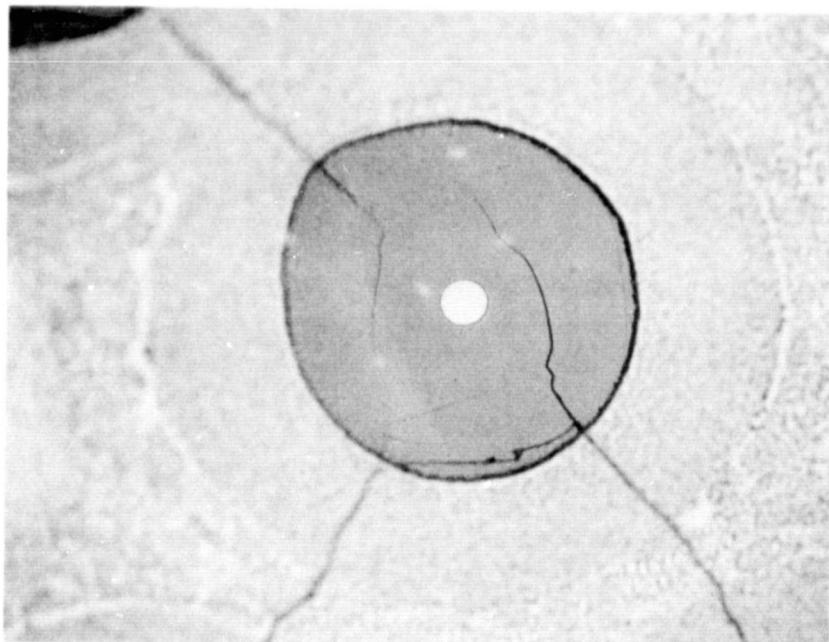
500 X

N-2437

FIG. 10 -- Microstructure of SiC/Hastelloy X composite after HIP
2 hours at 1825°F (996°C), 15,000 psi



100 X



500 X

N-2439

FIG. 11 -- Microstructure of SiC/S57 composite after HIP 2 hours at
1825°F (996°C), 15,000 psi

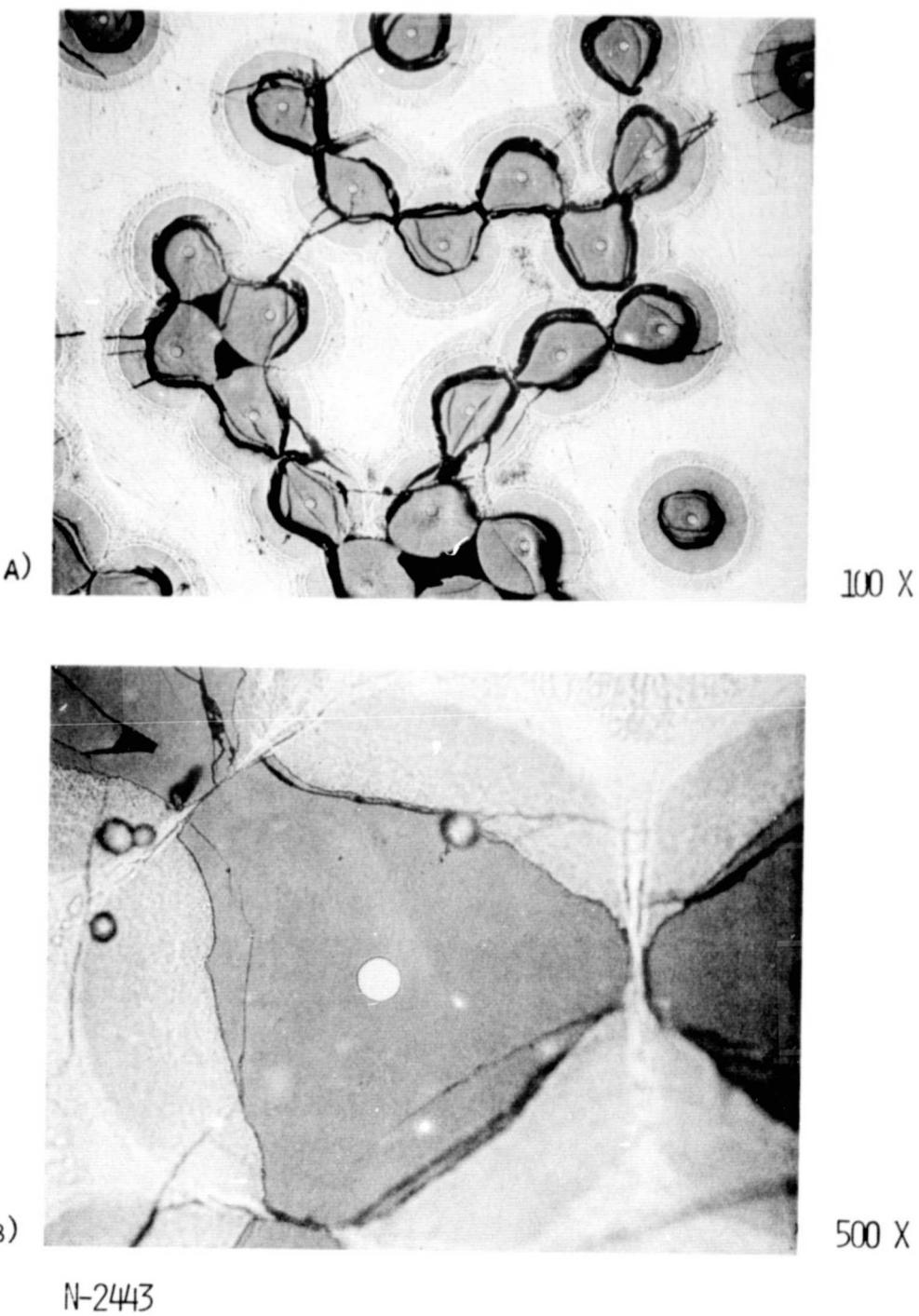
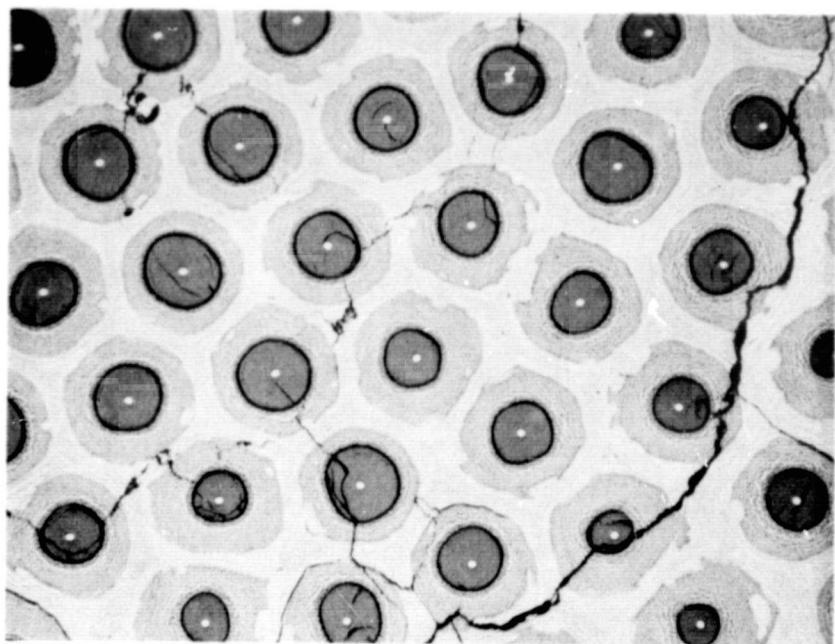
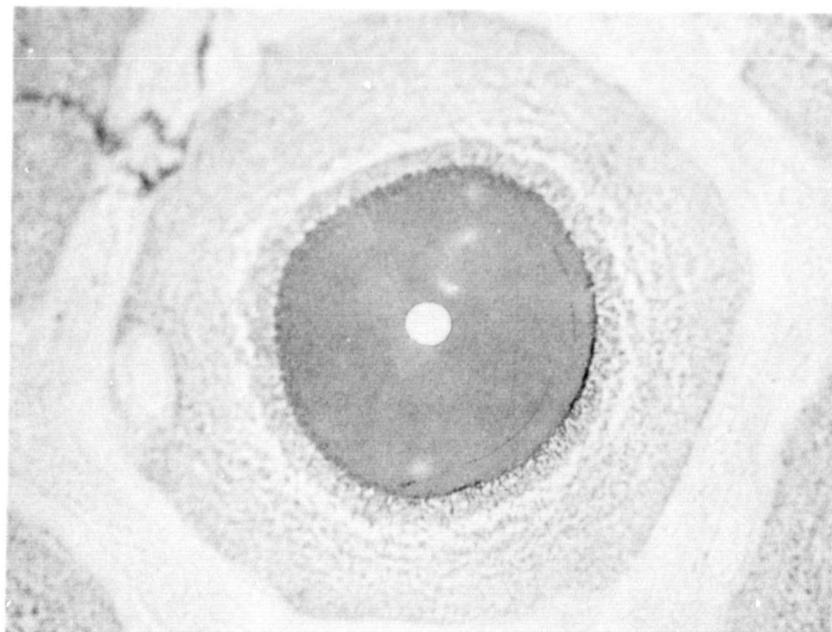


FIG. 12 -- Microstructure of SiC/NiCrAlY composite after HIP 2 hours
at 1825°F (996°C), 15,000 psi



100 X

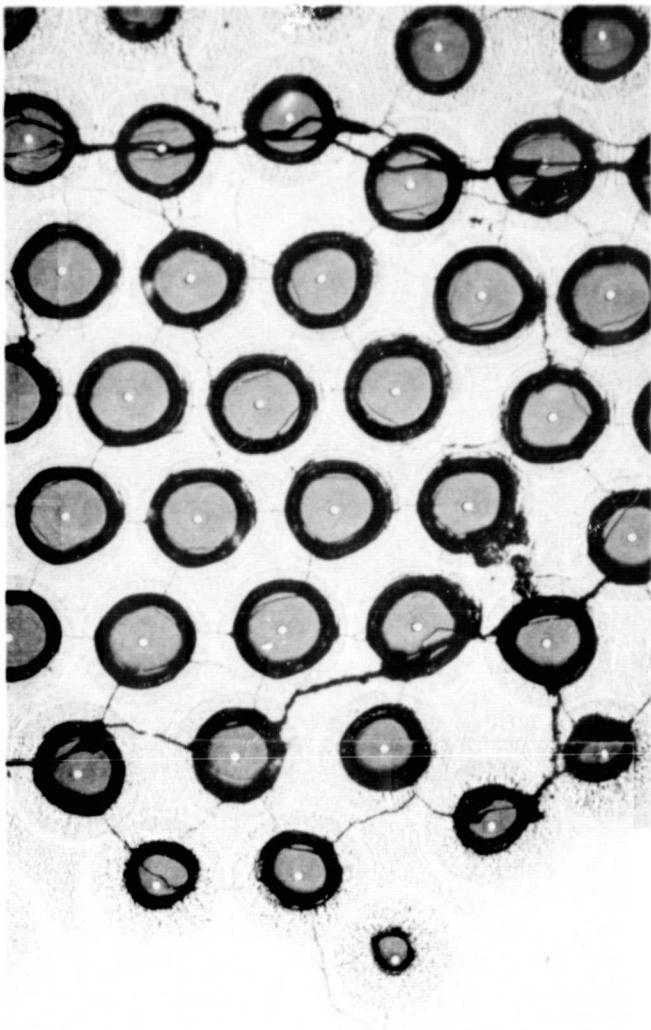


500 X

N-2440

FIG. 13 -- Microstructure of SiC/Incoloy 800 after HIP 2 hours at 1825°F (996°C), 15,000 psi

REPRODUCIBILITY OF THE
ORIGINAL PAGE IS POOR



N-2446

100 X

FIG. 14 -- Microstructure of SiC/FeCrAlY composite after HIP 2 hours at 1825°F (996°C), 15,000 psi. Note extensive dissolution and reaction of SiC fibers at edge of fiber pack

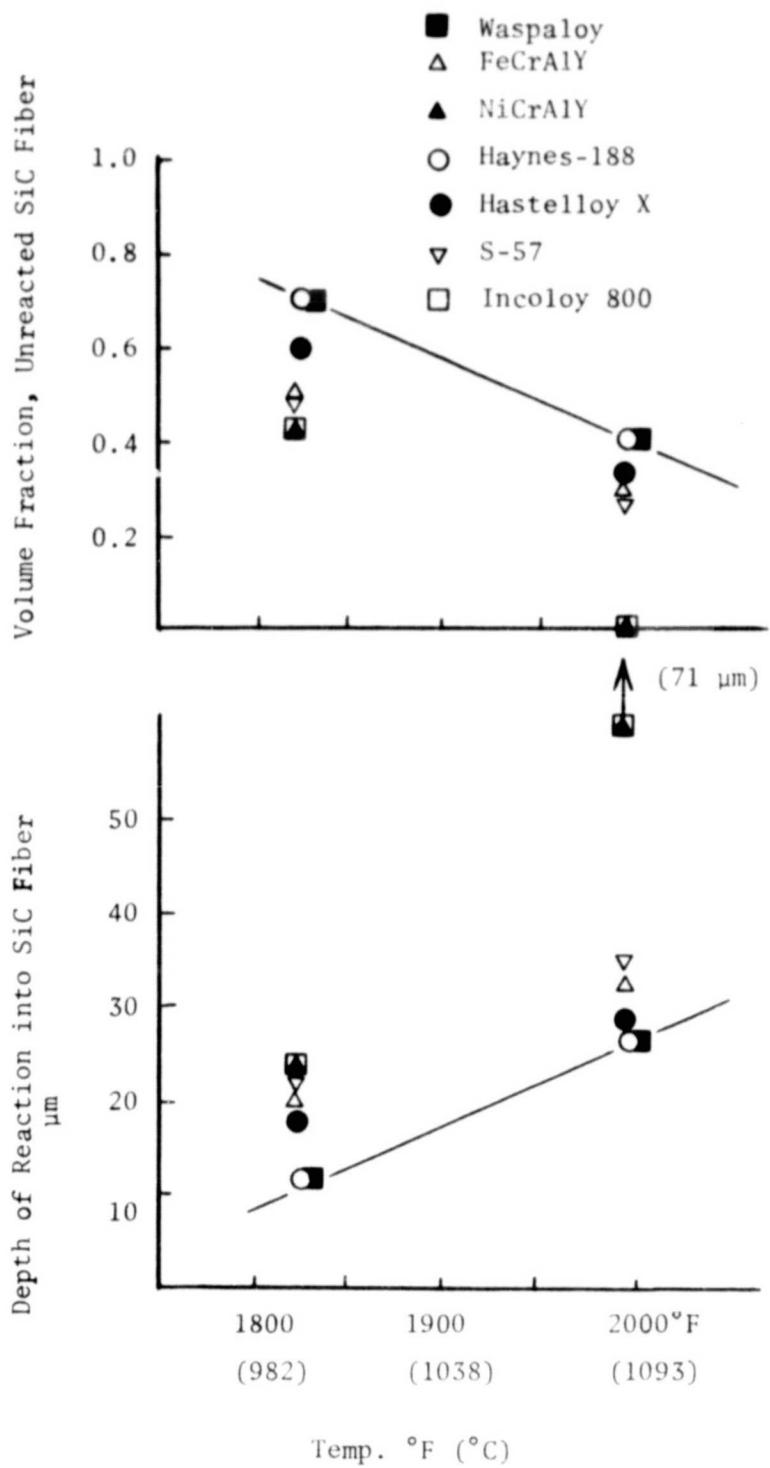
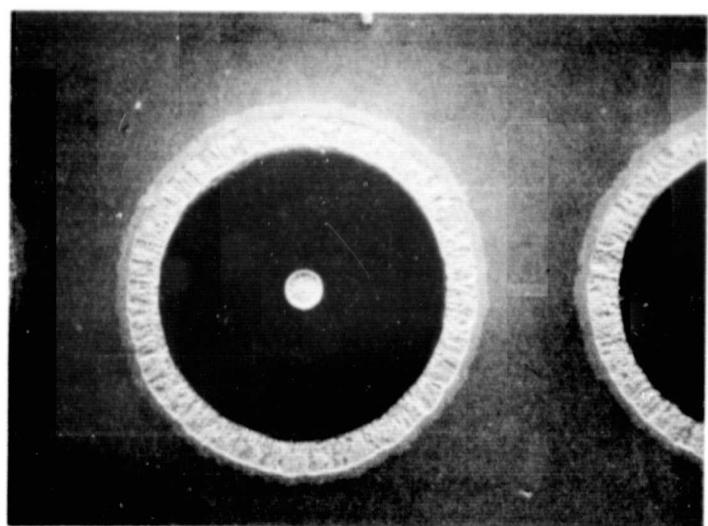
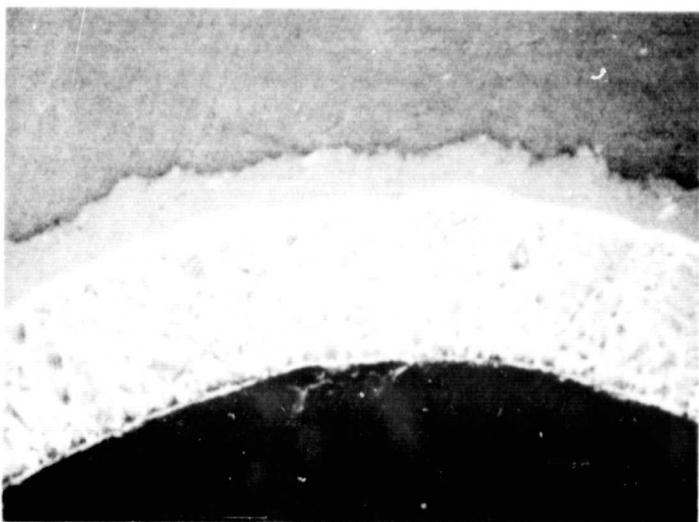


FIG. 15 -- DEPTH OF REACTION AND VOLUME FRACTION OF UNREACTED FIBER AS A FUNCTION OF HIP TEMPERATURE (2 HOURS HOLD TIME, 103 MPa (15,000 PSI))

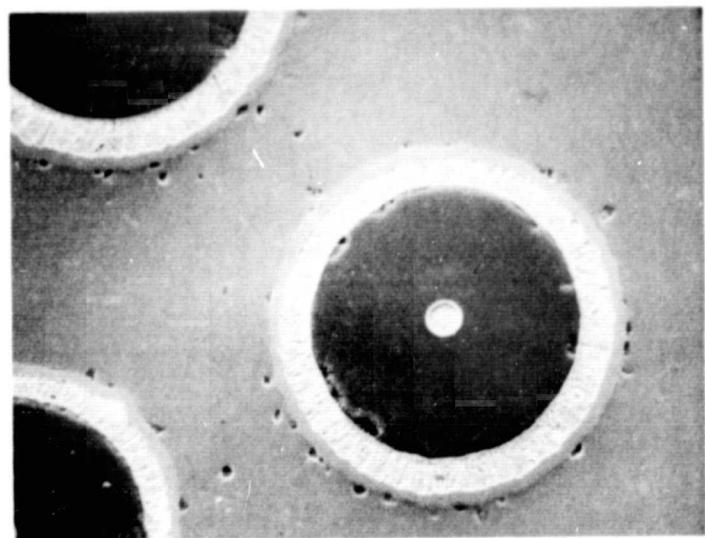


400 X

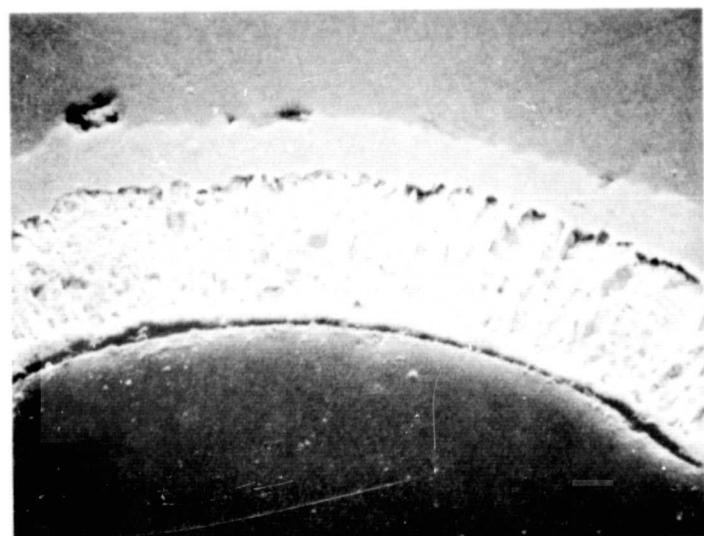


2000 X

FIG. 16 -- Chemical interaction between Waspaloy and CVD W coated SiC after 200 hours at 1800°F (982°C)



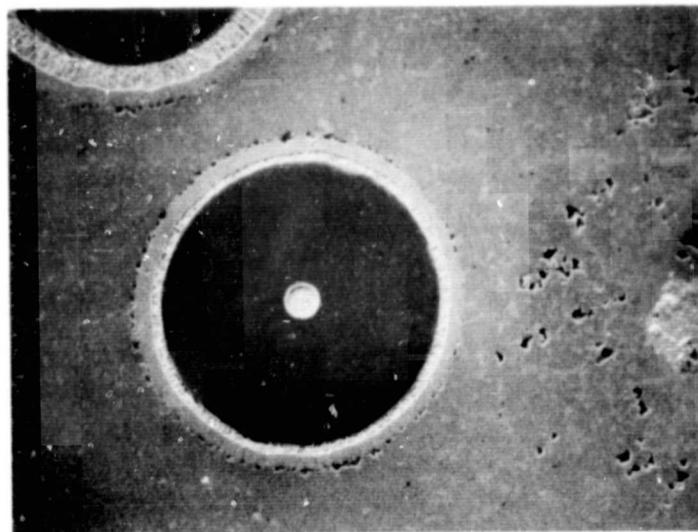
400 X



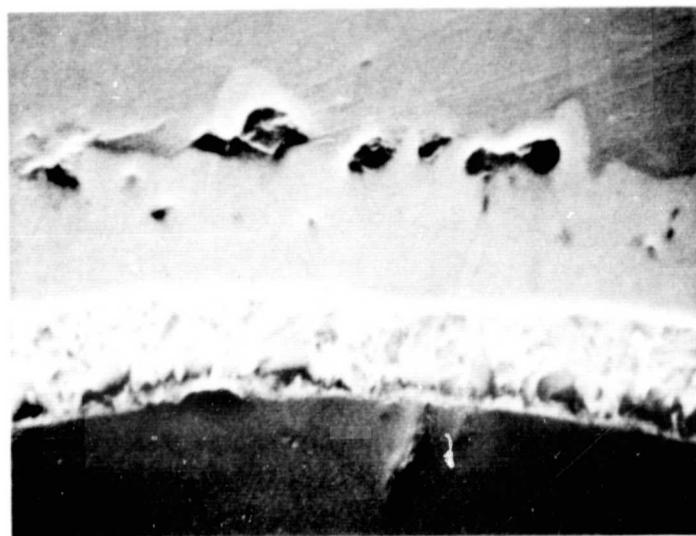
2000 X

FIG. 17 -- Chemical interaction between Hastelloy X and CVD W coated SiC after 200 hours at 1800°F (982°C)

REPRODUCIBILITY OF THE
ORIGINAL PAGE IS POOR



400 X



4000 X

FIG. 18 -- Chemical interaction between Haynes Alloy 188 and CVD W coated SiC after 200 hours at 1800°F (982°C)

Curve 655272-A

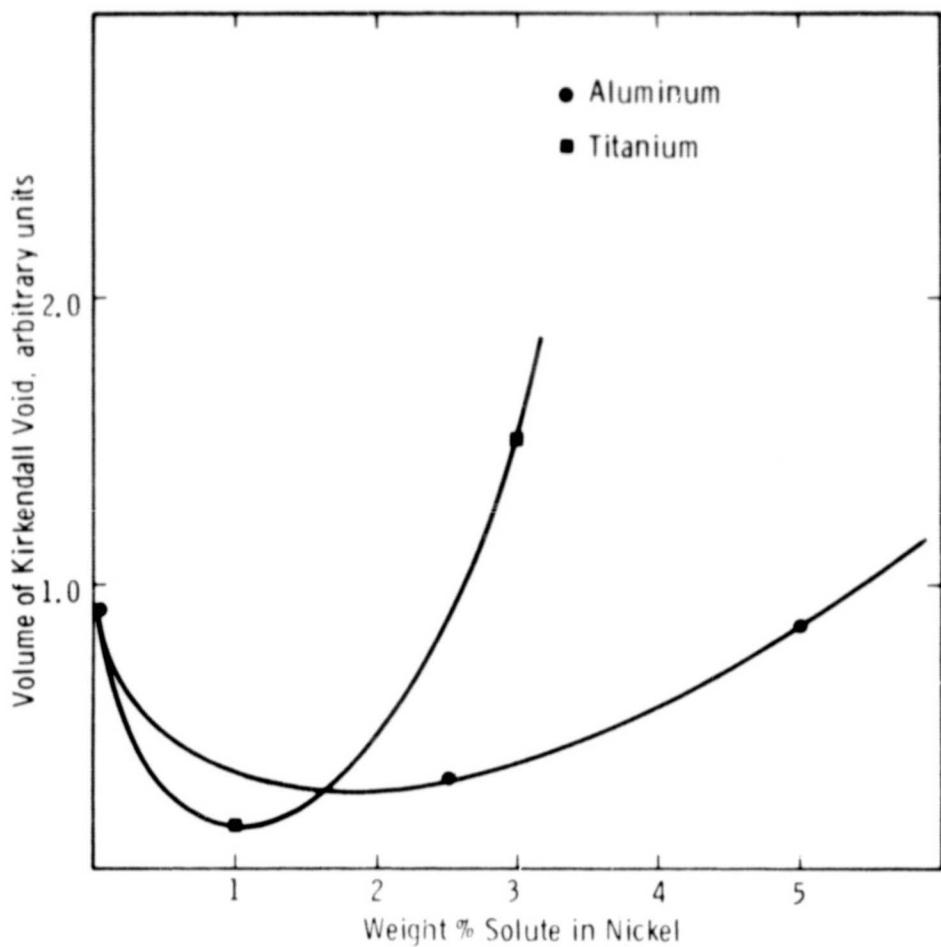


FIG. 19 -- Kirkendall void formation in binary matrix/W-2ThO₂ composites versus matrix solute content after 100 hours at 1150°C (2100°F). Aluminum and titanium solute additions

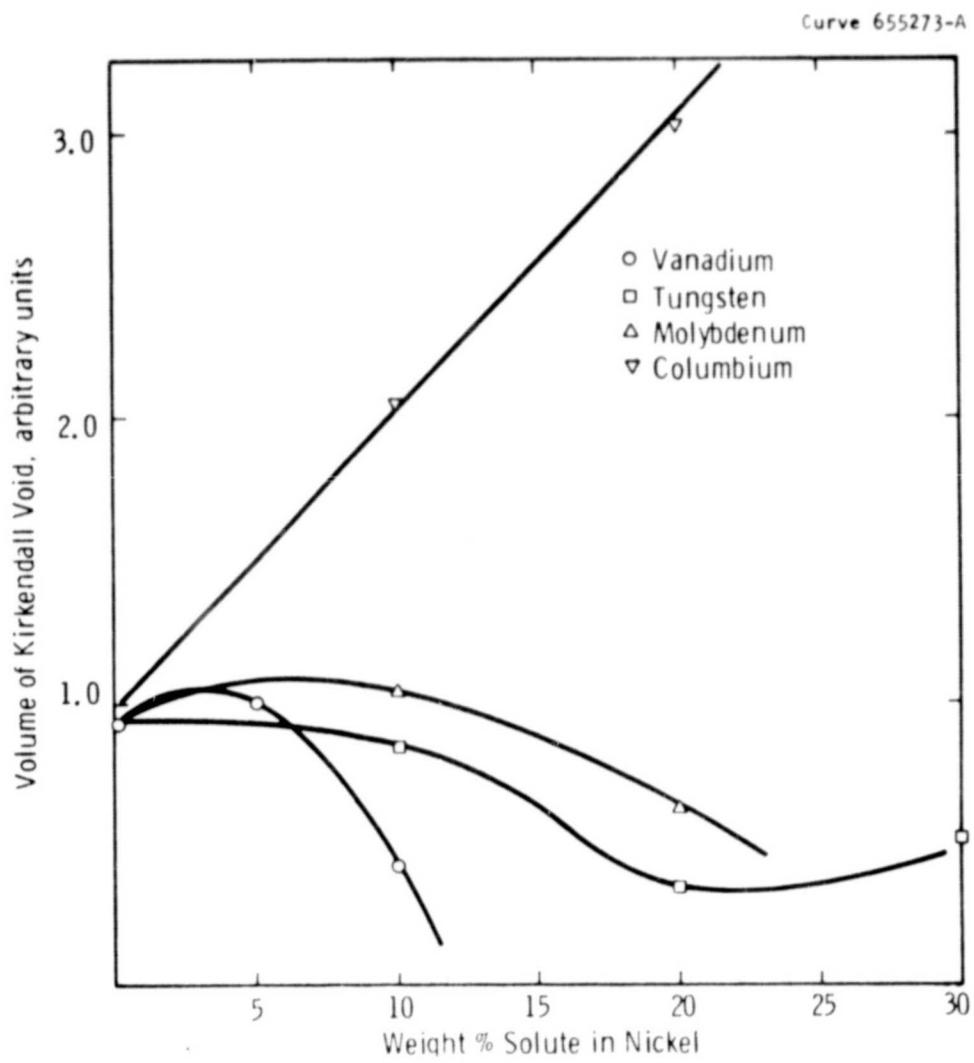


FIG. 20 -- Kirkendall void formation in binary matrix/W-2ThO₂ composites versus matrix solute content after 100 hours at 1150°C (2100°F). Vanadium, tungsten, molybdenum and columbium solute additions

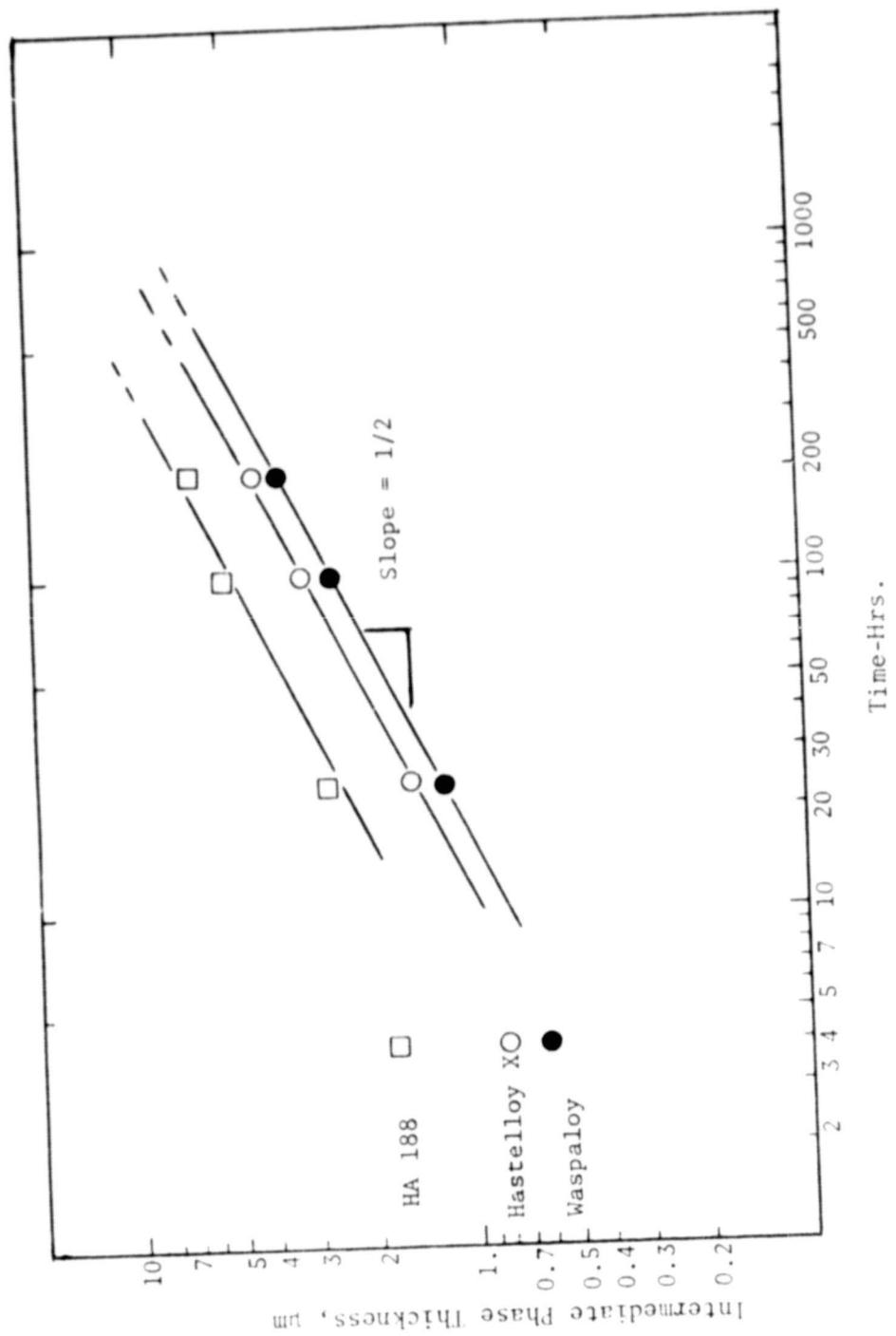
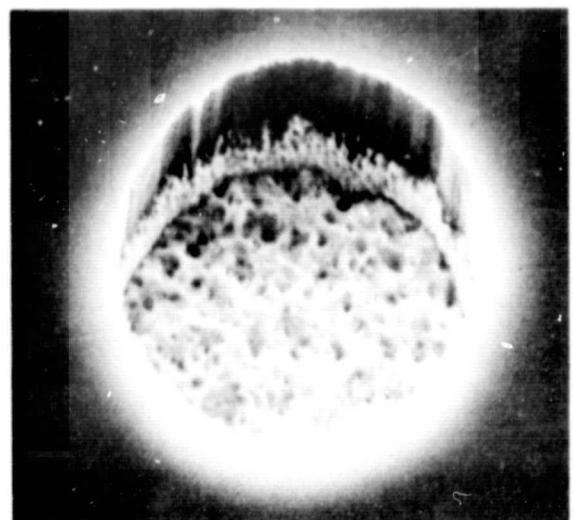
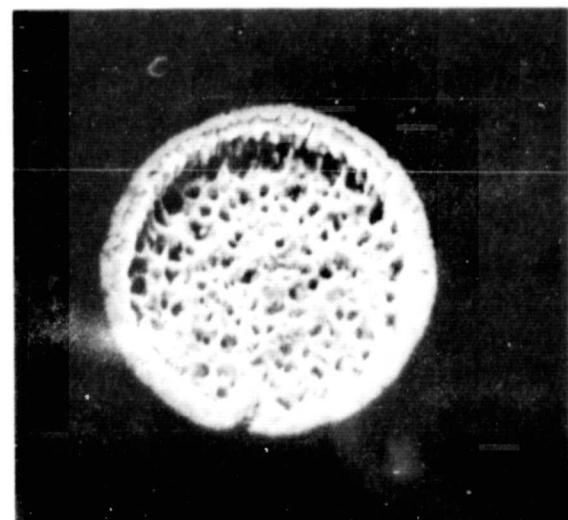


FIG. 21 -- Growth kinetics of intermediate phase between candidate matrix alloys and CVD tungsten coated SiC at 982°C (1800°F)



4000 X

4 hr. at 1800°F



4000 X

200 hr. at 1800°F

FIG. 22 -- Growth of intermediate phases between tungsten core and SiC at 1800°F

REPRODUCIBILITY OF THE
ORIGINAL PAGE IS POOR

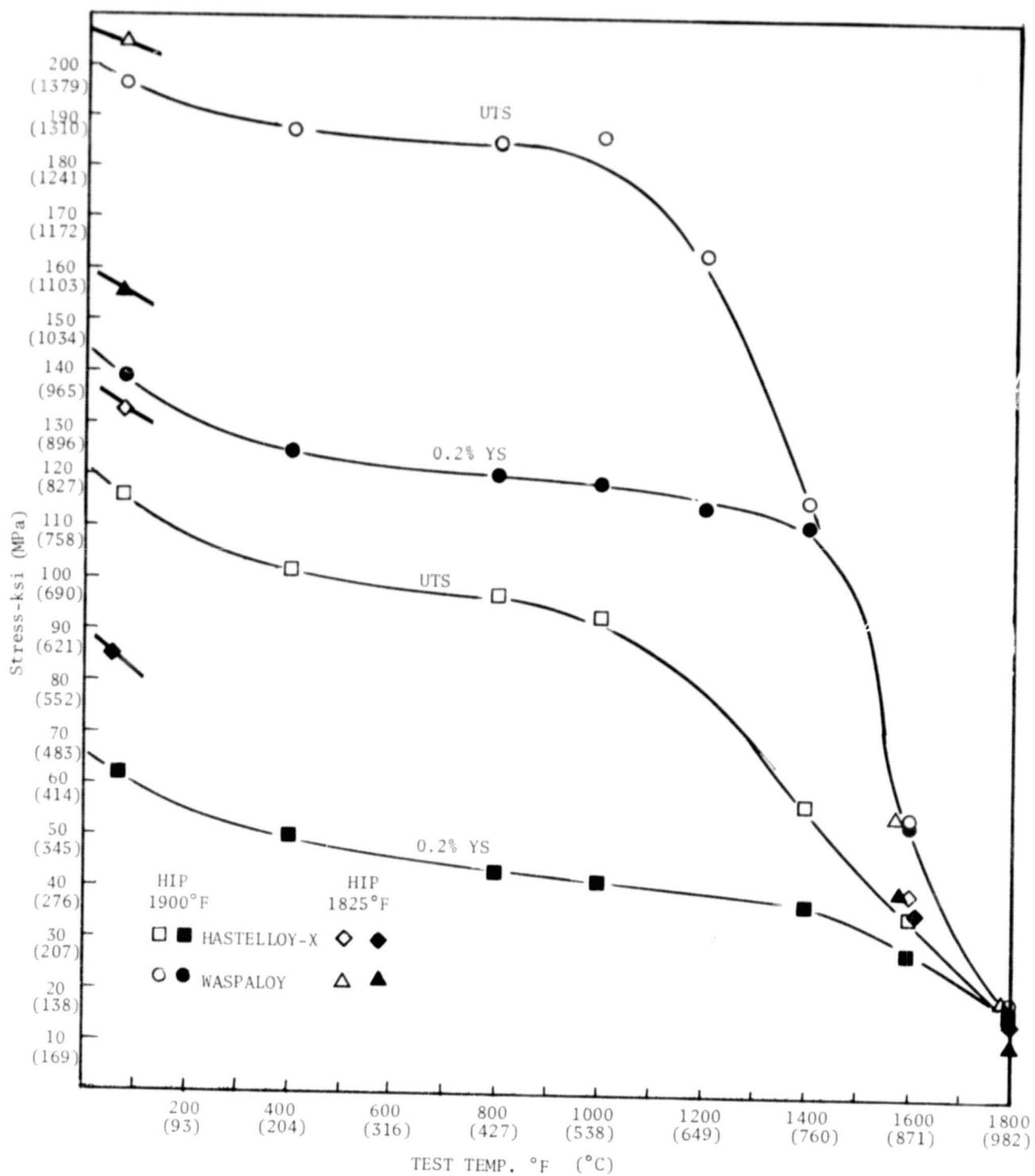


FIG.23 -- Tensile strength of Hastelloy-X and Waspaloy (PM HIP at 1038°C (1900°F)) as a function of test temperature.

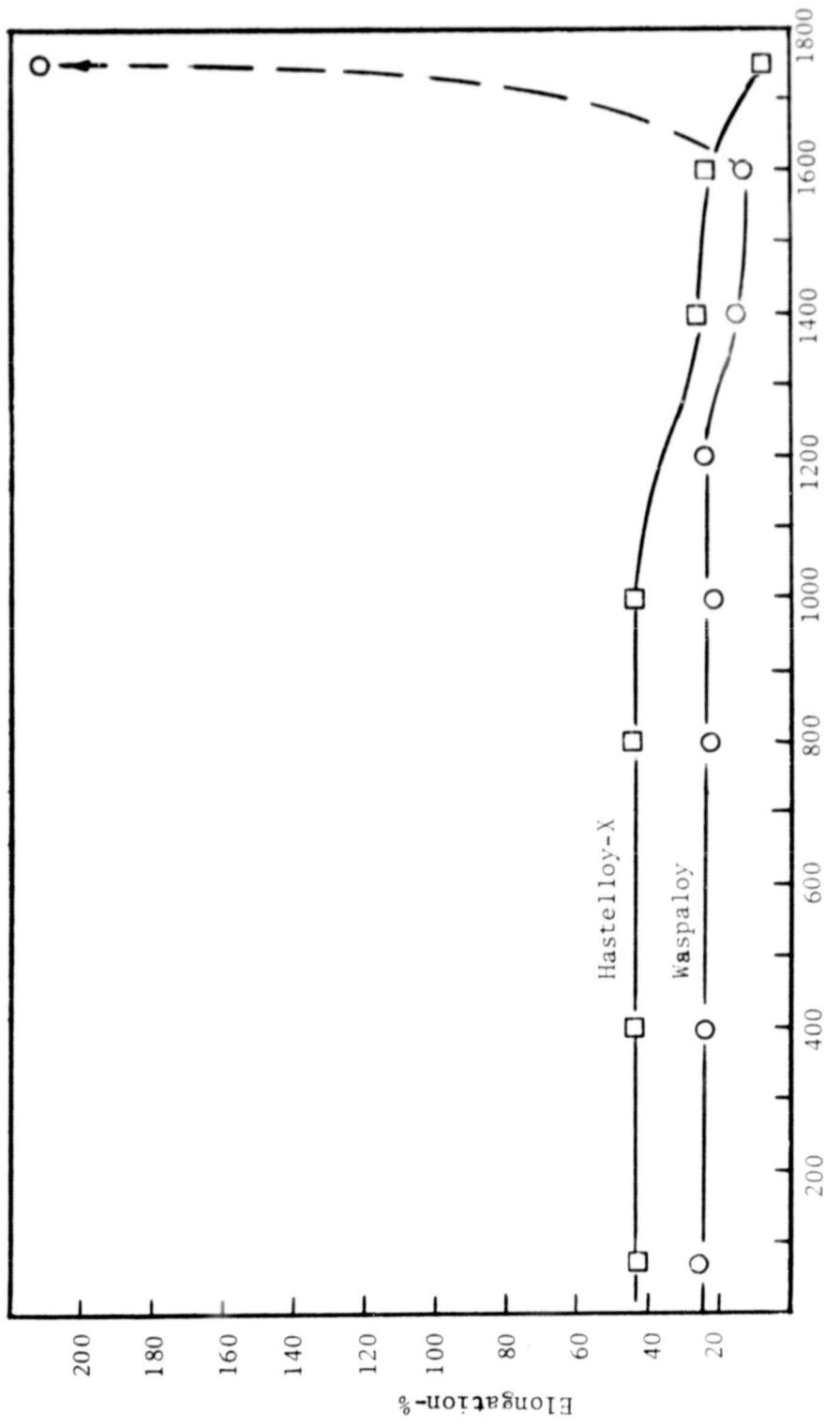


FIG. 24 -- Ductility of PM/HIP Hastelloy-X and Waspaloy as a function of temperature (strain rate = 0.05 min)



FIG. 25 -- Waspaloy HIP consolidated at 1038°C (1900°F). Tensile tested at 871°C (1600°F). Longitudinal section near fracture

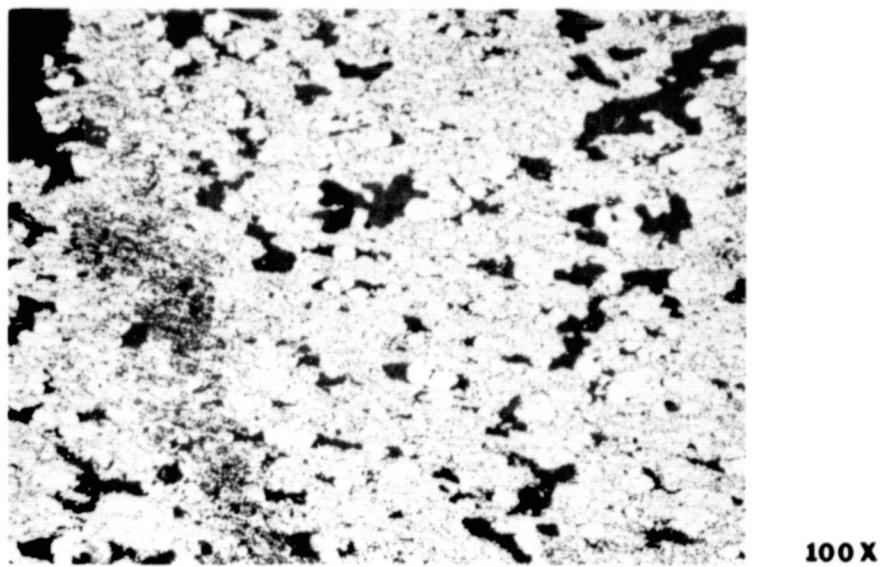
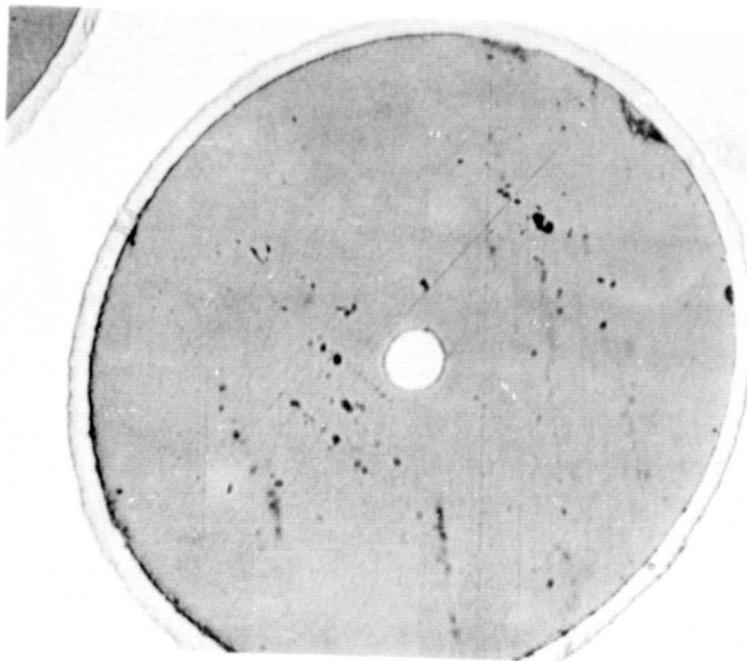
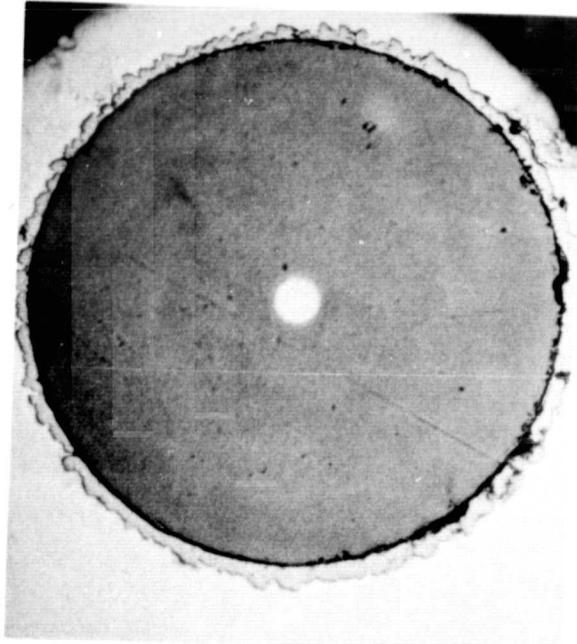


FIG. 26 -- Waspaloy HIP consolidated at 1038°C (1900°F). Tensile tested at 982°C (1800°F). Longitudinal section near fracture

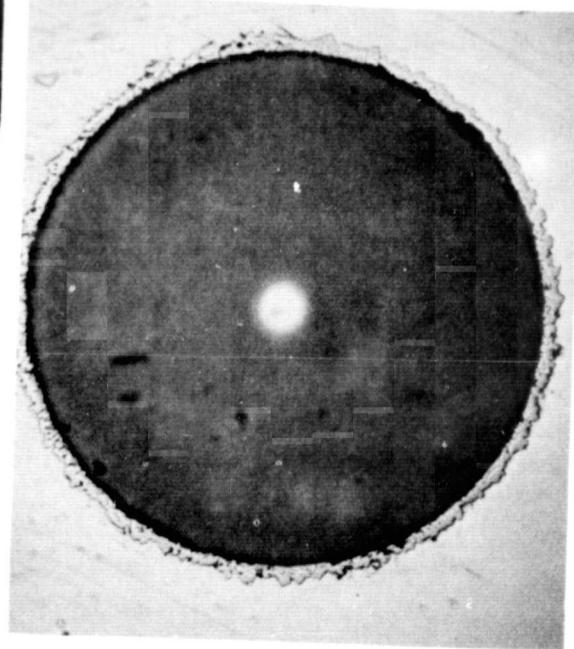
REPRODUCIBILITY OF THE
ORIGINAL PAGE IS POOR



S-662



8S69



8S80

FIG. 27 -- CVD tungsten coated SiC fibers. Matrix
is electroplated Ni

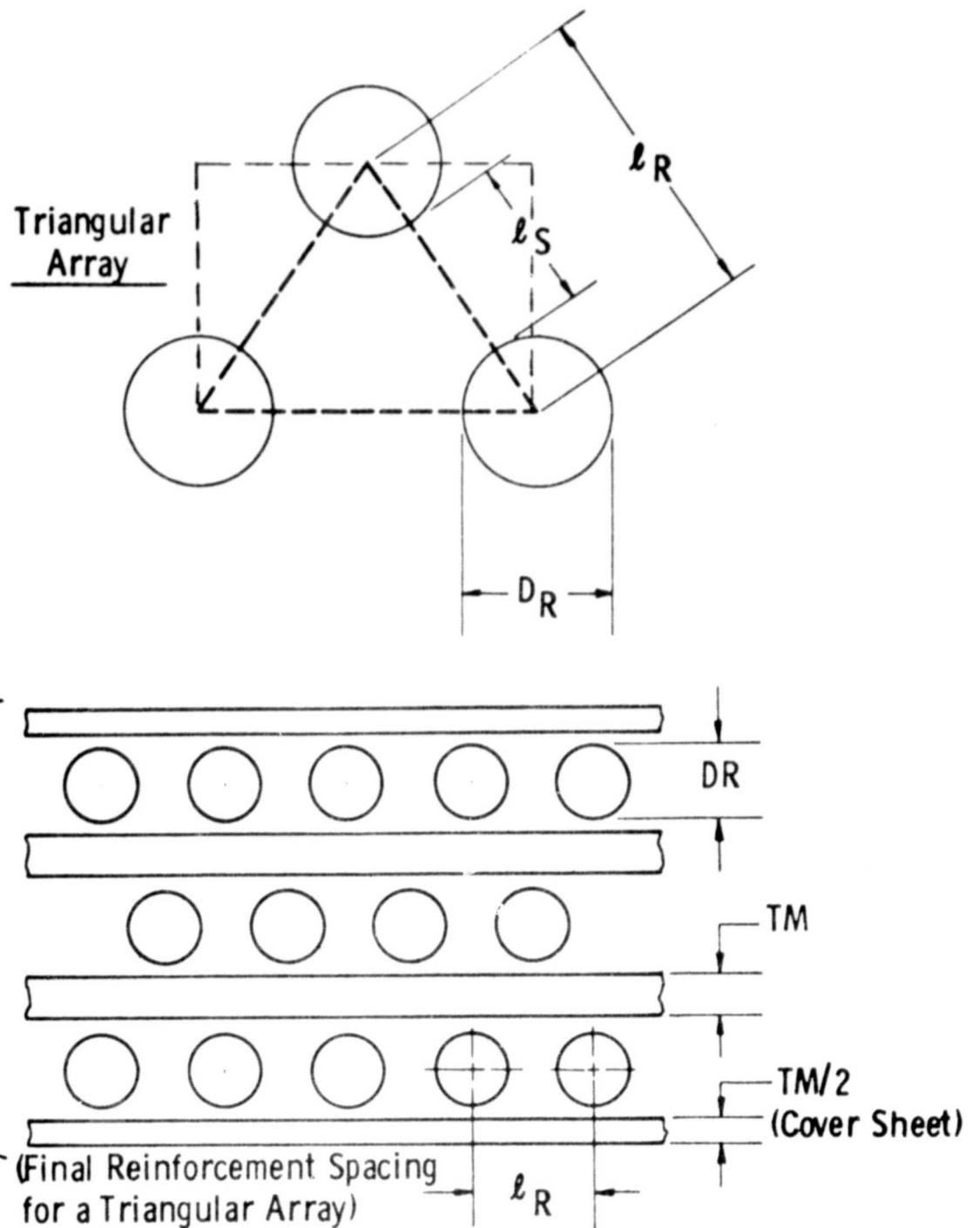
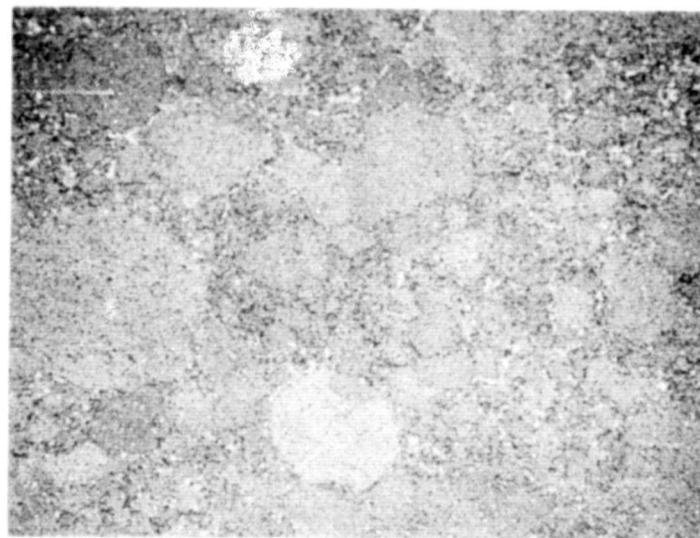


FIG. 28 -- Schematic of reinforcement spacing and lay-up for composite production from matrix foil (or powder tape and reinforcement mats - triangular array)



500 X



3300 X

FIG. 29 -- SEM photomicrograph of Mar-M-200 alloy prepared by HIP*
Vita-tape (binder removed prior to evacuation and sealing
of capsule)

* HIP at 2200°F (1204°C) at 15,000 psi

REPRODUCIBILITY OF THE
ORIGINAL PAGE IS POOR

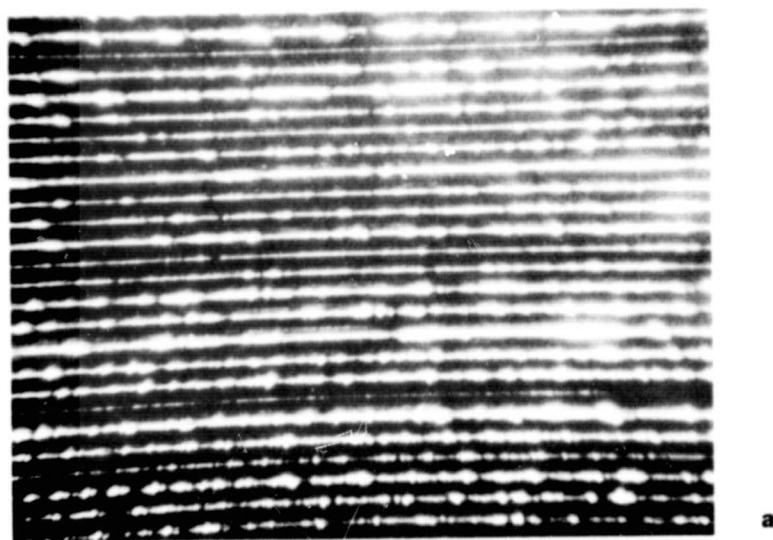


500 X



3100 X

FIG. 30 -- SEM photograph of Mar-M-200 alloy prepared by HIP at 2050°F (1121°C), 15,000 psi, post HIP heat treatment - 1 hr. at 2200°F (1204°C) powder from same lot as in Vita-tape



a



b

FIG. 31 -- Winding irregularities in acrylic sprayed fiber mat (a), guillotine sheared edge (b).

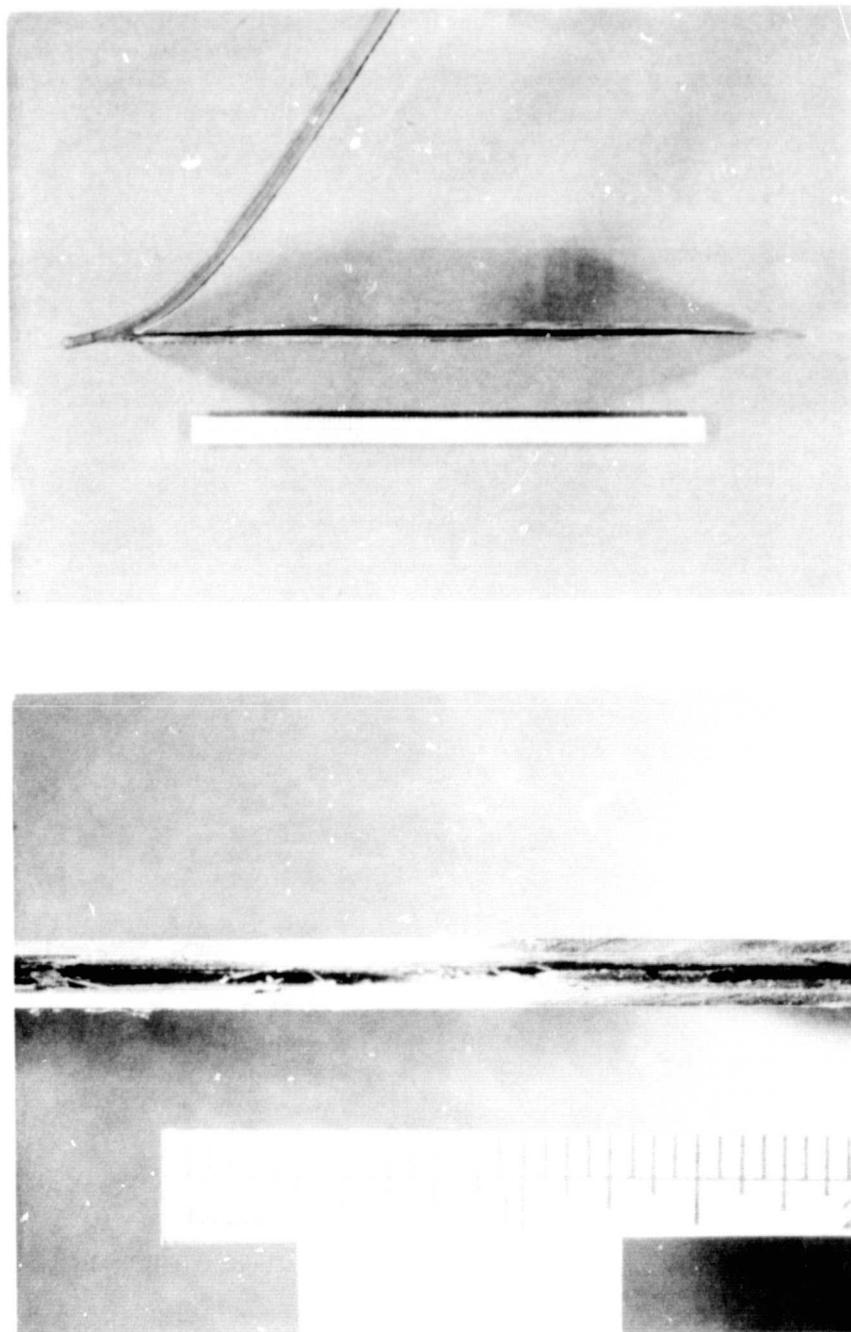


FIG. 32 -- Delamination of composite panel upon longitudinal sectioning

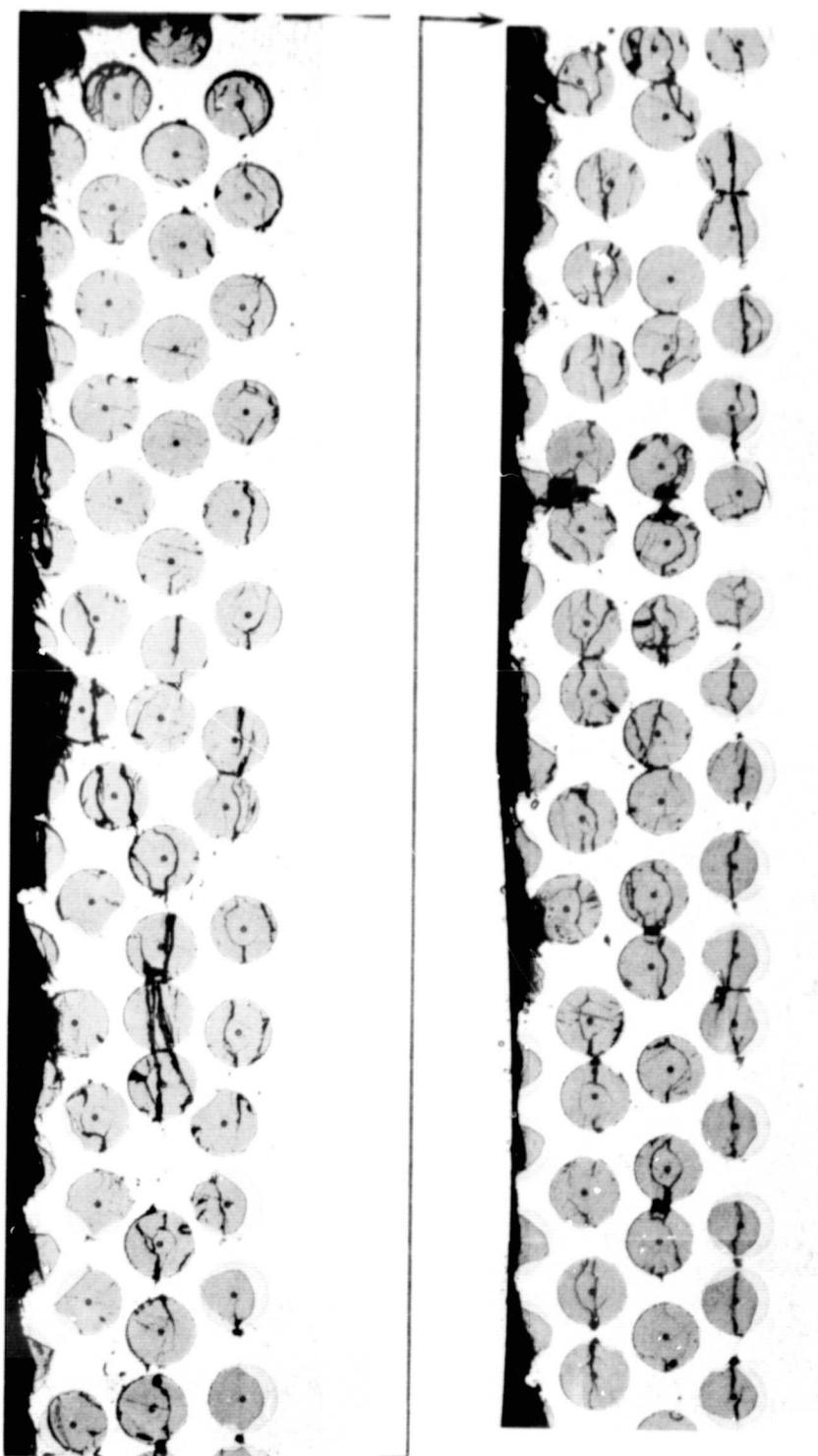
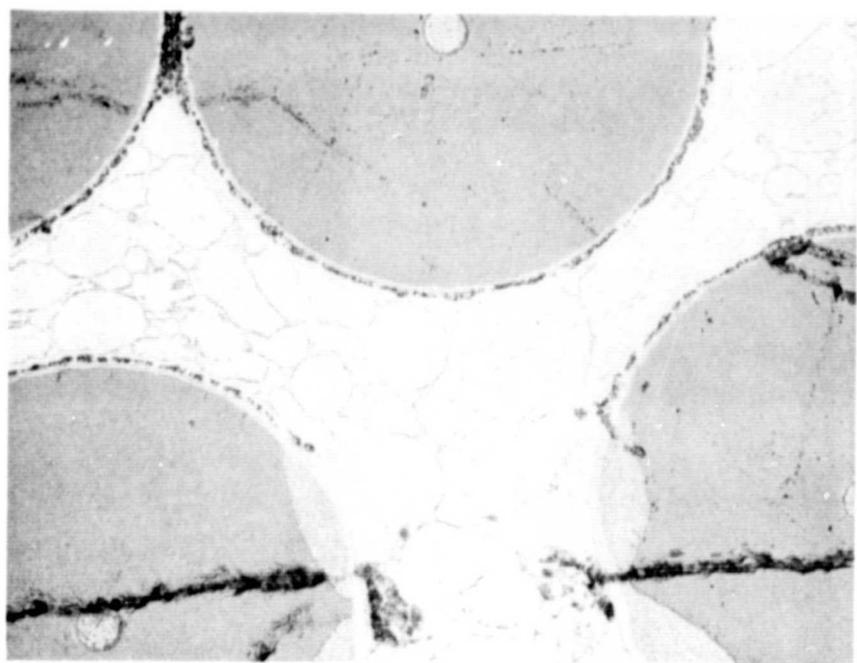
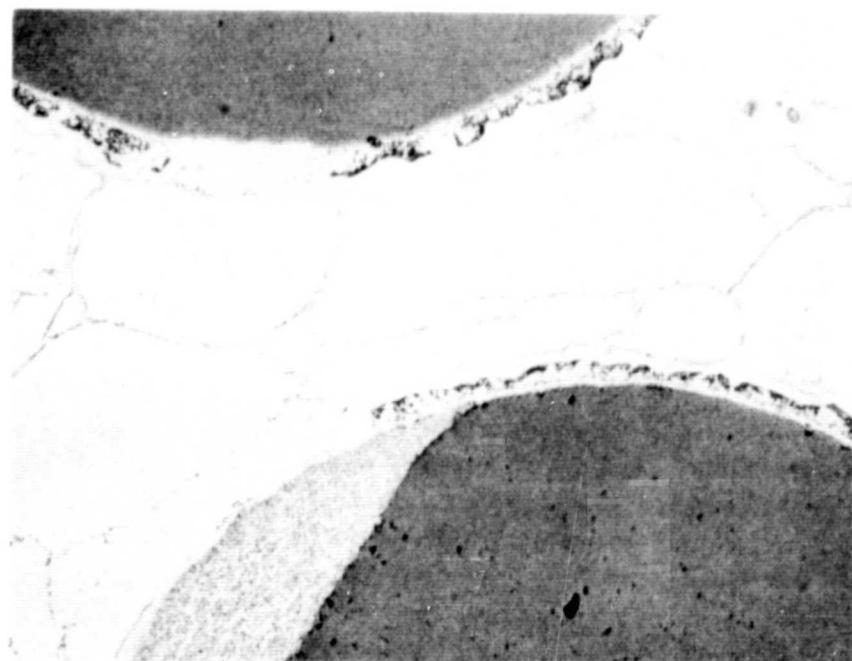


FIG. 33 -- Photomicrograph of delaminated specimen fiber lot 8S80

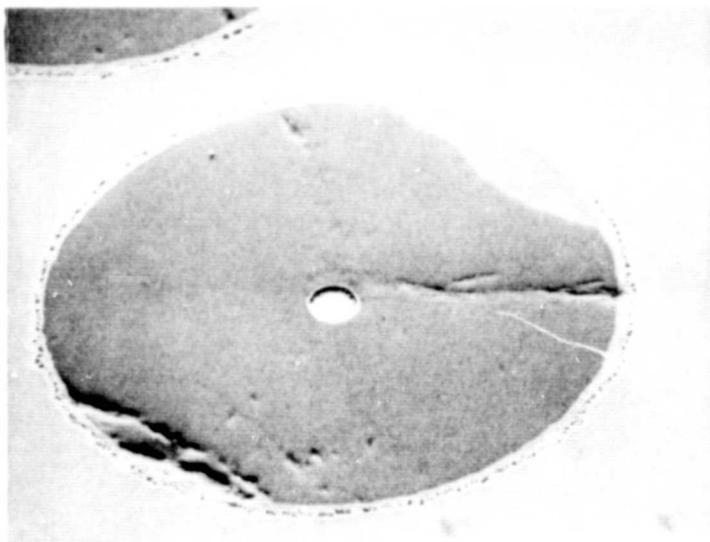


500X

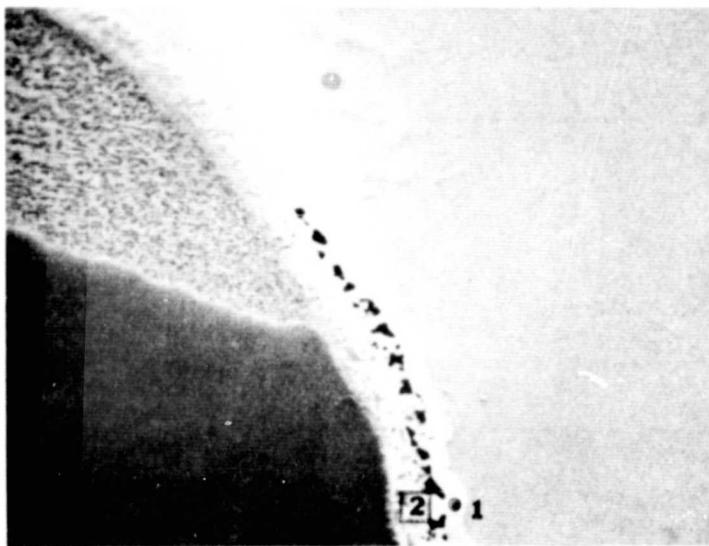


1000 X

FIG. 34 -- Fiber/matrix interactions through CVD tungsten barrier during 2 hr. at 1900°F (1040°C) HIP (filament lot 8S80)

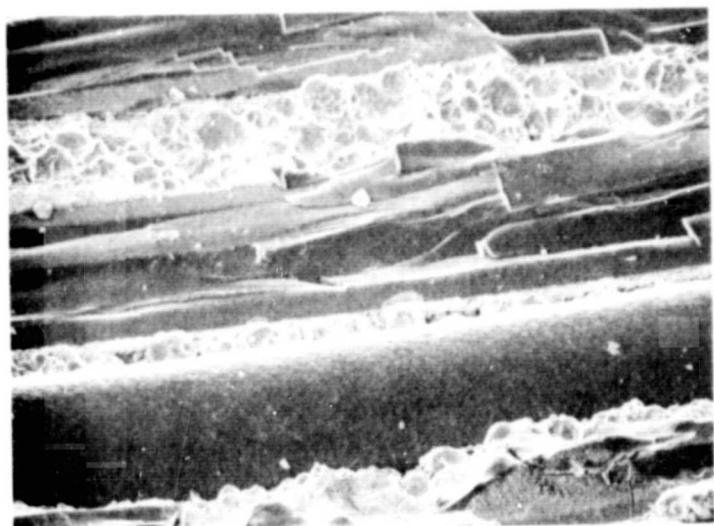


575X

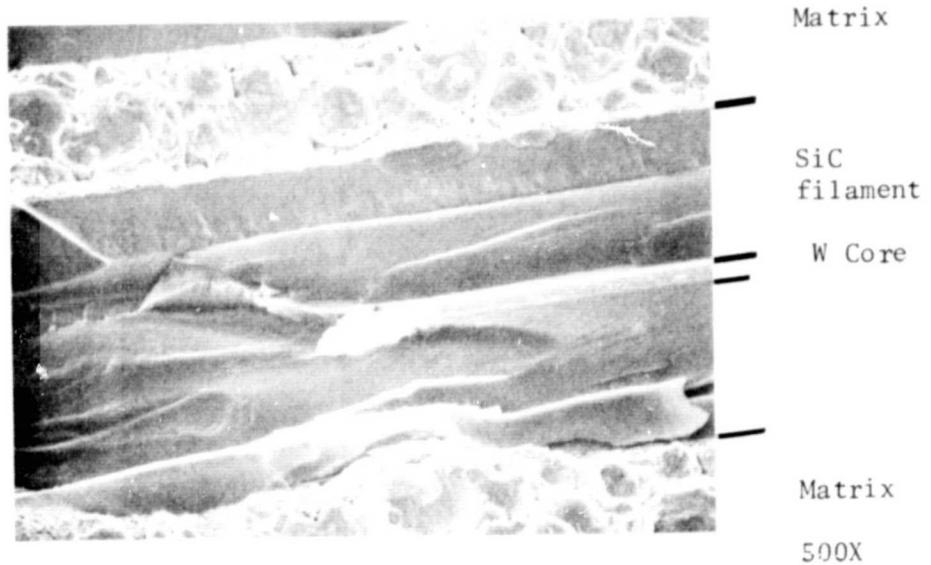


2300X

FIG. 35 -- SEM photomicrograph of Lot 8S80 CVD W-coated fiber after 2 hr. HIP consolidation at 1039°C (1900°F) 20 ksi (137 MPa) in a Waspaloy matrix

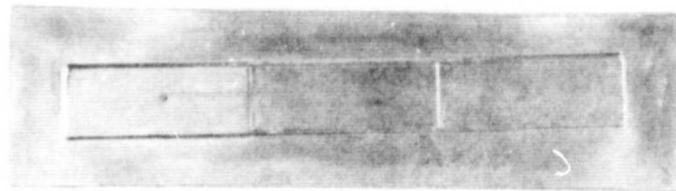
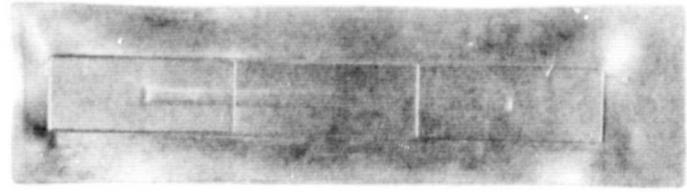


200X



500X

FIG. 36 -- SEM photomicrograph of delamination fracture surface of composite panel



10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60

FIG. 37 -- Composite test panels and resulting high temperature test specimens

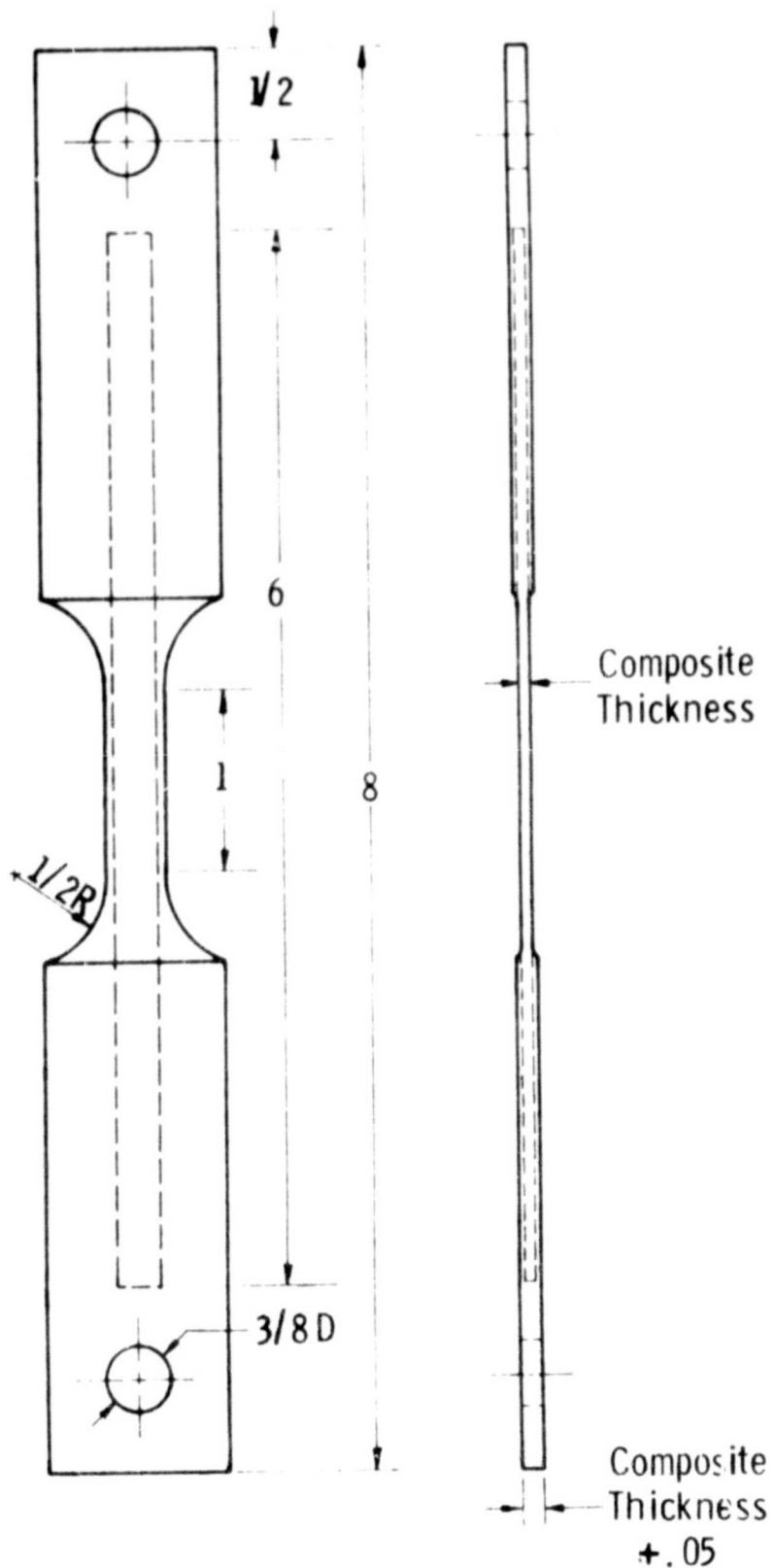


FIG. 38 -- High temperature composite tensile specimen
(Indicated dimensions in inches)

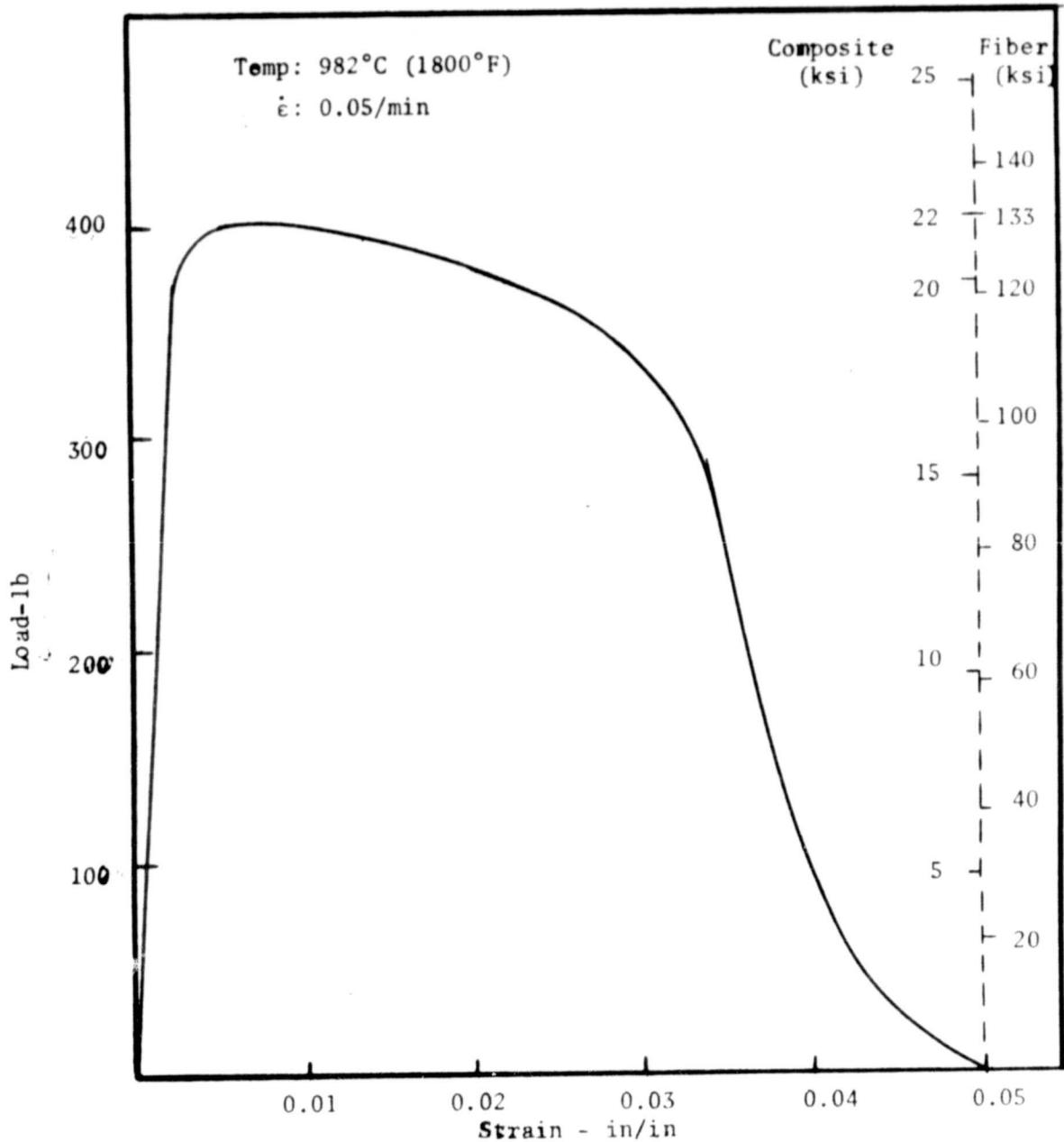


FIG. 39 -- Stress-strain curve for composite specimen DP 28B tested at 982°C (1800°F)

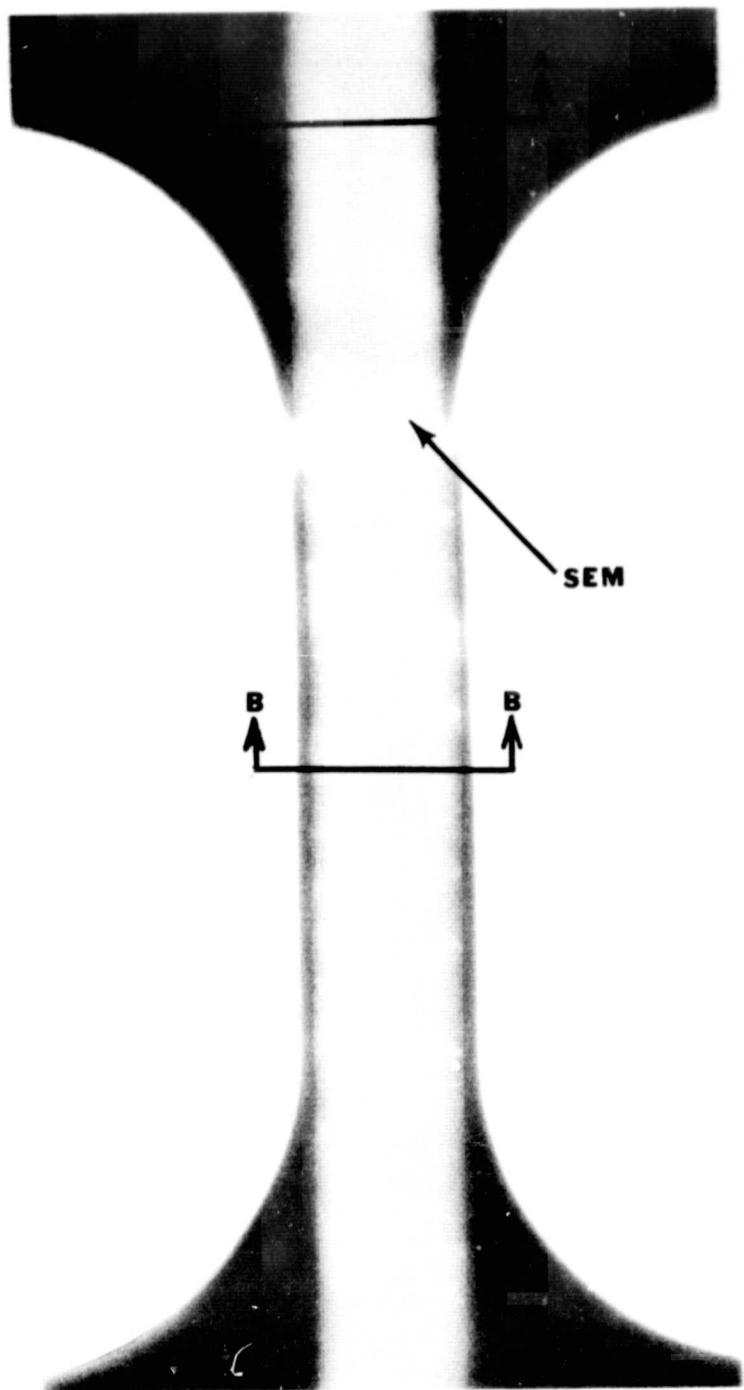


FIG. 40 -- Radiograph of SiC filament/Waspaloy composite test specimen no. DP 28B after tensile testing at $\epsilon = 0.05$ in/in/min

REPRODUCIBILITY OF THE
ORIGINAL PAGE IS POOR

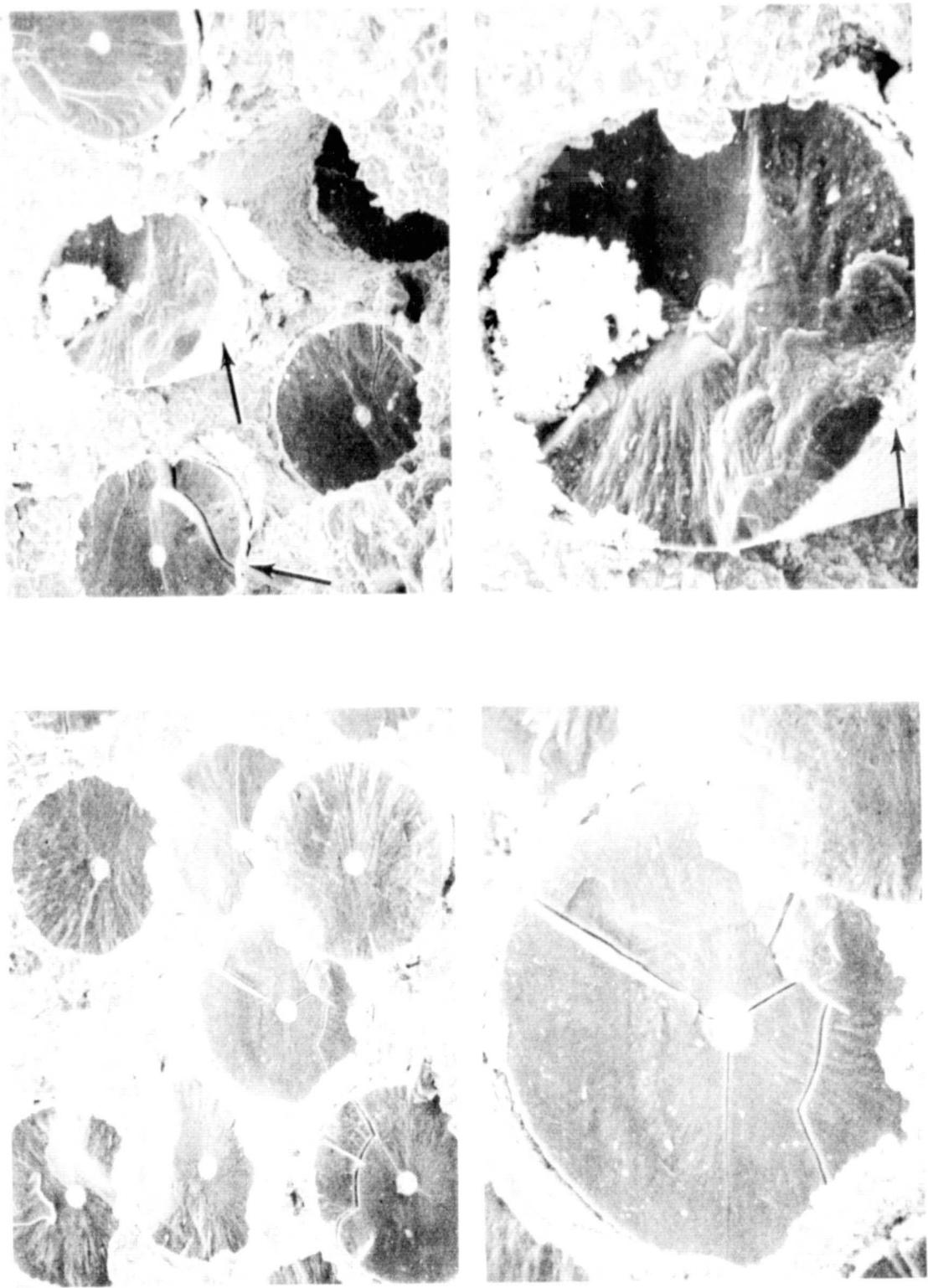


FIG. 41 -- SEM photographs of fracture of specimen DP 28B after 1800°F tensile test. Note matrix/filament interaction (arrows) (fiber lot 8S80 HIP at 1825°F)